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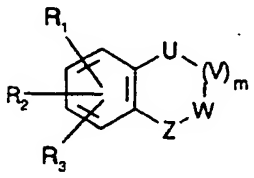
Description

[0001] The present invention relates to new antidotes, their use as antidotes in herbicidal compositions, these compositions and their usage in the control of grasses and weeds in cultivations of useful plants, especially in cultivations of maize, cereals, soybeans and rice.

[0002] The objects of the present invention are compounds of formula I

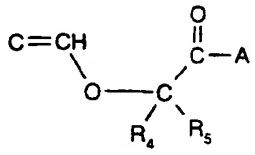


(I),

wherein

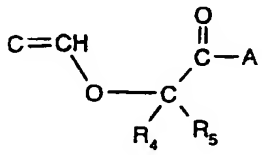
R_1 is hydrogen, C_1-C_4-alkyl, C_1-C_4-alkyl substituted by C_1-C_4-alkyl-X- or C_1-C_4-halogen-alkyl-X-, C_1-C_4-halogen-alkyl, nitro, cyano, -$COOR_8$, -NR_9R_{10}, -$SO_2NR_{11}R_{12}$ or -$CONR_{13}R_{14}$;
R_2 is hydrogen, halogen, C_1-C_4-alkyl, trifluoromethyl, C_1-C_4-alkoxy or C_1-C_4-halogen-alkoxy;
R_3 is hydrogen, halogen or C_1-C_4-alkyl;
U, V, W and Z, independently of one another, are oxygen, sulphur, $C(R_{15})R_{16}$, carbonyl, NR_{17} or

a group



with the provisos that

a) at least one of the ring members U, V, W or Z is carbonyl, and one ring member which is adjacent to this or these ring members signifies the group

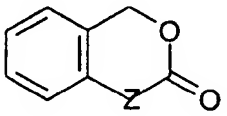


whereby this group only appears once; and

b) two adjacent ring members U and V, V and W and W and Z cannot simultaneously signify oxygen;
R_4 and R_5, independently of one another, signify hydrogen or C_1-C_8-alkyl; or
R_4 and R_5 together form a C_2-C_6-alkylene group;
A is R_7-Y- or -$NR_{18}R_{19}$;
X is oxygen or -$S(O)_p$;
Y is oxygen or sulphur;
R_7 is hydrogen, C_1-C_8-alkyl, C_1-C_8-halogen-alkyl, C_1-C_4-alkoxy-C_1-C_8-alkyl, C_3-C_6-alkenyloxy-C_1-C_8-alkyl or phenyl-C_1-C_8-alkyl, whereby the phenyl ring may be substituted by halogen, C_1-C_4-alkyl, trifluoromethyl, methoxy or methyl-$S(O)_p$-; C_3-C_6-alkenyl, C_3-C_6-halogen-alkenyl, phenyl-C_3-C_6-alkenyl, C_3-C_6-alkinyl, phenyl-C_3-C_6-alkinyl, oxetanyl, furfuryl or tetrahydrofurfuryl;

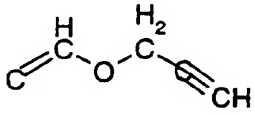
R_8 is hydrogen or C_1-C_4-alkyl;
R_9 is hydrogen, C_1-C_4-alkyl or C_1-C_4-alkylcarbonyl;
R_{10} is hydrogen or C_1-C_4-alkyl; or
R_9 and R_{10} together form a C_4- or C_5-alkylene group;
R_{11}, R_{12}, R_{13} and R_{14}, independently of one another, are hydrogen or C_1-C_4-alkyl; or R_{11} together with R_{12} or R_{13} together with R_{14}, independently of one another, are C_4- or C_5-alkylene, whereby one carbon atom may be replaced by oxygen or sulphur, or one or two carbon atoms may be replaced by -NR_{15}-;
R_{15} and R_{16}, independently of one another, are hydrogen or C_1-C_8-alkyl; or
R_{15} and R_{16} together are C_2-C_6-alkylene;
R_{17} is hydrogen, C_1-C_8-alkyl, optionally substituted phenyl or benzyl optionally substituted on the phenyl ring;
R_{18} is hydrogen, C_1-C_8-alkyl, phenyl, phenyl-C_1-C_8-alkyl, whereby the phenyl rings may be substituted by fluorine, chlorine, bromine, nitro, cyano, -OCH_3, C_1-C_4-alkyl or CH_3SO_2-; C_1-C_4-alkoxy-C_1-C_8-alkyl, C_3-C_6-alkenyl, C_3-C_6-alkinyl or C_3-C_6-cycloalkyl;
R_{19} is hydrogen, C_1-C_8-alkyl, C_3-C_6-alkenyl or C_3-C_6-alkinyl; or
R_{18} and R_{19} together are C_4- or C_5-alkylene, whereby one carbon atom may be replaced by oxygen or sulphur, or one or two carbon atoms may be replaced by -NR_{20}-;
R_{20} is hydrogen or C_1-C_4-alkyl;
m is 0 or 1; and
p signifies 0, 1 or 2,

the compounds of formula I_{01a}

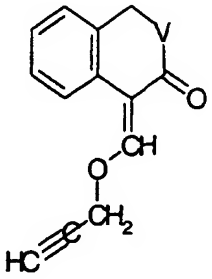


(I_{01a}),

wherein Z is a group C=CH-O,-CH_2CH=CH_2,

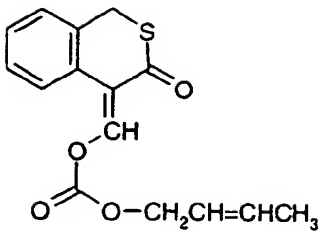


or C=CH-O-C(O)OCH_2CH=$CHCH_3$,
the compounds of formula I_{01b}

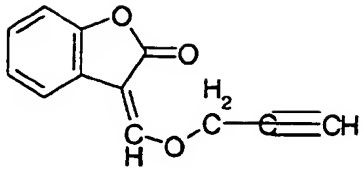


(I_{01b}),

wherein V is sulfur or NCH_3, and the 4 individual compounds no. 01.161

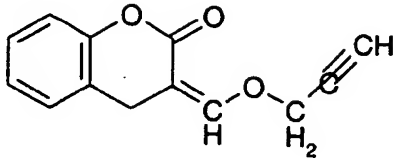


(01.161), 02.002

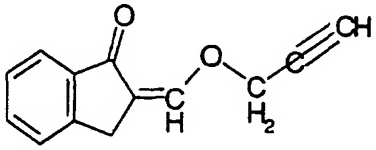


(02.002),

03.001



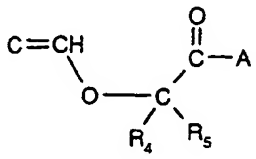
(03.001) and 04.003



(04.003),

as well as agronomically compatible salts and stereoisomers of these compounds.

[0003] The proviso a) denotes compounds of formula I, wherein 1, 2 or 3 of the ring members U, V, W and/or Z, independently of one another, are carbonyl, and one ring member which is adjacent thereto is the group



This group itself appears only once in the compound of formula I. Therefore, in the proviso a), "one" is the numeral.

[0004] In the above-mentioned definitions, halogen is understood to be iodine and preferably fluorine, chlorine and bromine.

[0005] The alkyl, alkenyl and alkinyl groups appearing in the definitions of the substituents may be straight-chain or branched, and the same applies also to the alkyl, alkenyl and alkinyl moiety of the alkylcarbonyl, alkoxyalkyl, alkylthio and alkylsulphonyl groups.

[0006] Alkyl groups denote for example methyl, ethyl, n-propyl, iso-propyl, n-butyl, sec.-butyl, isobutyl, tert.-butyl, as well as the various isomeric pentyl, hexyl, heptyl and octyl radicals. Methyl, ethyl, n-propyl, iso-propyl and n-butyl are preferred.

[0007] Examples of alkenyls which may be mentioned are allyl, methallyl, 1-methylvinyl, but-2-en-1-yl, pentenyl and 2-hexenyl, preferably alkenyl radicals with a chain length of 3 to 5 carbon atoms.

[0008] Examples of alkinyls which may be mentioned are propargyl, 1-methylpropargyl, 3-butinyl, but-2-in-1-yl, 2-methylbut-3-in-2-yl, but-3-in-2-yl, 1-pentinyl, pent-4-in-1-yl and 2-hexinyl, preferably alkinyl radicals with a chain length of 3 to 5 carbon atoms.

[0009] The halogen-alkyl which may be considered are alkyl groups that are substituted by halogen once or many times, especially once to three times, whereby halogen signifies in detail iodine and especially fluorine, chlorine and bromine, for example fluoromethyl, difluoromethyl, trifluoromethyl, chloromethyl, dichloromethyl, trichloromethyl, 2-fluoroethyl, 2,2-difluoroethyl, 2-chloroethyl, 2,2-dichloroethyl, 2,2,2-trifluoroethyl and 2,2,2-trichloroethyl.

[0010] Alkylsulphonyl is for example methylsulphonyl, ethylsulphonyl, propylsulphonyl, isopropylsulphonyl, n-butyl-

sulphonyl, iso-butylsulphonyl, sec.-butylsulphonyl and tert.-butylsulphonyl; preferably methylsulphonyl and ethylsulphonyl.

[0011] Halogen-alkylsulphonyl is for example fluoromethylsulphonyl, difluoromethylsulphonyl, trifluoromethylsulphonyl, chloromethylsulphonyl, trichloromethylsulphonyl, 2-fluoroethylsulphonyl, 2,2,2-trifluoroethylsulphonyl and 2,2,2-trichloroethylsulphonyl.

[0012] Alkylcarbonyl is especially acetyl and propionyl.

[0013] Alkoxy is for example methoxy, ethoxy, n-propoxy, iso-propoxy, n-butoxy, iso-butoxy, sec.-butoxy and tert.-butoxy.

[0014] Alkenyloxy is for example allyloxy, methallyloxy and but-2-en-1-yloxy.

[0015] Alkinyloxy is for example propargyloxy and 1-methylpropargyloxy.

[0016] Alkoxyalkyl is for example methoxymethyl, methoxyethyl, ethoxymethyl, ethoxyethyl, n--propoxymethyl, n-propoxyethyl, iso-propoxymethyl and iso-propoxyethyl.

[0017] Halogenalkoxy is for example fluoromethoxy, difluoromethoxy, trifluoromethoxy, 2,2,2-trifluoroethoxy, 1,1,2,2-tetrafluoroethoxy, 2-fluoroethoxy, 2-chloroethoxy and 2,2,2-trichloroethoxy.

[0018] Of the alkenyl radicals that are substituted 1, 2 or 3 times by halogen, preference is given to those which have a chain length of 3 or 4 carbon atoms. The alkenyloxy groups may be substituted by halogen at saturated or unsaturated carbon atoms.

[0019] The halogen-alkenyloxy which may be considered are alkenyloxy groups that are substituted by halogen once or many times, whereby halogen signifies in detail bromine, iodine and especially fluorine and chlorine, for example 2- and 3-fluoropropenyloxy, 2- and 3-chloropropenyloxy, 2- and 3-bromopropenyloxy, 2,3,3-trifluoropropenyloxy, 2,3,3-trichloropropenyloxy, 4,4,4-trifluoro-but-2-en-1-yloxy and 4,4,4-trichloro-but-2-en-1-yloxy.

[0020] Alkylthio signifies for example methylthio, ethylthio, propylthio and butylthio, as well as the branched isomers thereof.

[0021] Phenyl or benzyl per se, or as part of a substituent, such as phenylalkyl or benzylamino, exist in optionally substituted form, in which case the substituents may be in ortho-, meta- or paraposition. Substituents are e.g. C_1-C_4-alkyl, C_1-C_4-alkoxy, halogen, C_1-C_4-halogen-alkyl or C_1-C_4-halogen-alkoxy.

[0022] Corresponding significances may also be assigned to the substituents in compound definitions, such as alkyl-Y, halogen-alkyl-Y, alkoxy-alkyl-Y, alkenyloxy-alkyl-Y, phenyl-alkyl-Y, alkenyl-Y, halogen-alkenyl-Y, phenyl-alkenyl-Y, phenyl-alkinyl-Y, halogen-alkyl-X-alkyl and alkyl-S(O)-alkyl.

[0023] In the definition of alkylcarbonyl, the carbonyl carbon atom is not included in the lower and upper numeric limits for carbon atoms respectively indicated.

[0024] Preference is given to compounds of formula I, wherein R_{17} is hydrogen or C_1-C_8-alkyl, and R_{18} is hydrogen, C_1-C_8-alkyl, phenyl, phenyl-C_1-C_8-alkyl, whereby the phenyl rings may be substituted by fluorine, chlorine, bromine, nitro, cyano, -OCH_3, C_1-C_4-alkyl or CH_3SO_2-; C_1-C_4-alkoxy-C_1-C_8-alkyl, C_3-C_6-alkenyl or C_3-C_6-alkinyl.

[0025] Preference is similarly given to compounds of formula I, wherein R_4 and R_5 are hydrogen.

[0026] Preference is also given to compounds of formula I, wherein A is R_7-Y-.

[0027] Of these compounds, preference is given in particular to those in which Y is oxygen.

[0028] Preferred compounds of formula I are also those in which U is $C(R_{15})R_{16}$.

[0029] Equally preferred compounds of formula I are those in which R_{15} and R_{16} signify hydrogen.

[0030] Equally preferred are compounds of formula I, wherein m is 1, and V is oxygen or sulphur.

[0031] Also preferred are compounds of formula I, wherein m is 0.

[0032] Further preferred are compounds of formula I, wherein R_1 to R_5 are hydrogen, m is 1, V is oxygen, U is $C(R_{15})R_{16}$ and A is R_7-Y-.

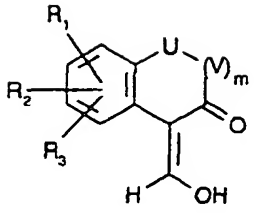
[0033] Of these, particular preference is given to those wherein R_{15} and R_{16} signify hydrogen, R_7 is methyl and Y is oxygen.

[0034] Important compounds of formula I are those wherein U is $C(R_{15})R_{16}$, m is 0, and R_1 to R_5 and A are defined as under formula I.

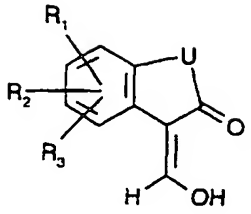
[0035] Of these, compounds that are particularly important are those in which R_1 to R_5, R_{15} and R_{16} are hydrogen, and A is R_7-Y-.

[0036] Of these, the compound in which R_7 is methyl and Y is oxygen is quite particularly important.

[0037] The process according to the invention for the production of compounds of formula I takes place analogously to known processes, and is characterised in that a compound of formula VIIa or VIIb

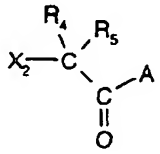


(VIIa) or



(VIIb),

wherein R_1 to R_3, U, V and m have the significances given under formula I,
is allowed to react with a compound of formula X



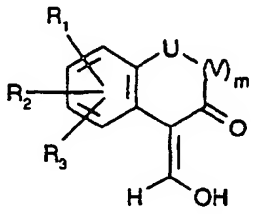
(X),

wherein R_4, R_5 and A have the significances given under formula I, and X_2 signifies a leaving group,

a) in the presence of a base and an organic solvent at temperatures of 0° to 100°C, or

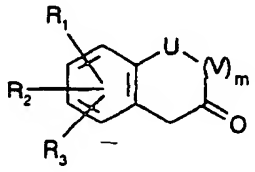
b) in the presence of an excess of cesium fluoride in an organic solvent at temperatures of 0° to 50°C.

[0038] The process according to the invention for the production of compounds of formula VIIa



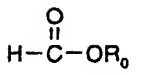
(VIIa),

wherein R_1 to R_3, U and V have the significances given under formula I and m is 1, takes place analogously to known processes, and is characterised in that a compound of formula XIa



(XIa),

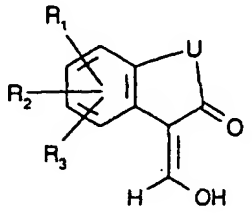
wherein R_1 to R_3, U, V and m have the significances indicated, is reacted with a compound of formula VIII



(VIII),

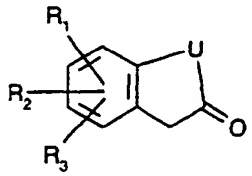
wherein R_0 is C_1-C_4-alkyl, in the presence of a base and optionally an organic solvent.

[0039] The process according to the invention for the production of compounds of formula VIIb



(VIIb),

wherein R_1 to R_3 and U have the significances given under formula I, and U is especially oxygen, takes place analogously to known processes, and is characterised in that a compound of formula XIb

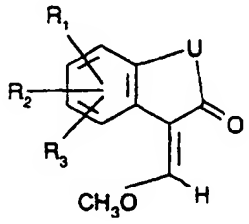


(XIb),

wherein R_1 to R_3 and U have the indicated significances, is reacted with a compound of formula IX

$$H\text{-}C(OCH_3)_3 \qquad \text{(IX)},$$

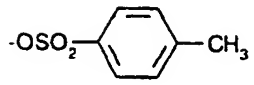
in the presence of an excess of acetic acid anhydride at an elevated temperature for 2 to 24 hours, to form the compound of formula VIIc



(VIIc)

and this compound undergoes enol ether cleavage with an aqueous base at 0° to 25°C, and is subsequently worked up under acidic conditions.

[0040] For the preparation of the compounds of formula I, e.g. the compounds of formula VIIa or VIIb may be reacted e.g. with an equimolar amount or an excess of reactive compound of formula X, whereby X_2 signifies a leaving group, for example halogen, especially chlorine or bromine, or $-OSO_2CH_3$ or



[0041] According to method a), this reaction takes place in an inert organic solvent, such as N,N-dimethylformamide (DMF), dichloromethane, tetrahydrofuran, dioxane, benzene, toluene, xylenes, dimethyl sulphoxide (DMSO) or diethylether in the presence of a base at temperatures of 0° to 100°C. Suitable bases are for example sodium or potassium hydride, butyl lithium, alcoholates e.g. sodium methylate, sodium ethylate, sodium i-propylate, sodium amylate or sodium t-butylate, trialkylamines e.g. triethylamine or tributylamine, N,N-dialkylated anilines, sodium amide ($NaNH_2$), sodium-bis-trimethylsilyl amide ($NaN(TMS)_2$), potassium-bis-trimethylsilyl amide ($KN(TMS)_2$) or lithium-bis-trimethylsilyl amide ($LiN(TMS)_2$).

[0042] According to method b), the above reaction is effected e.g. analogously to Synlett 1995, 843, in the presence of an excess (2 equivalents) of cesium fluoride in an inert organic solvent such as N,N-dimethylformamide at temperatures from 0° to 50°C, preferably 0° to 25°C.

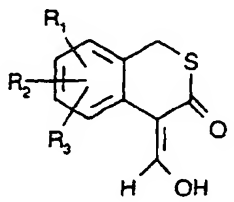
This process b) is especially suitable for reactive and towards bases unstable starting compounds.

[0043] The starting compounds of formula VIIa (m=1) and VIIb (m=0) may be produced analogously to known processes, e.g. the former in accordance with the general reaction conditions of a Claisen condensation, as described for example in Houben-Weyl, volume VIII, pages 560-590; ibid, volume VII/2a, pages 492, 495, 535 and 580; and ibid, volume VI/1d, pages 40ff. and page 275, as well as Z. Anal. Chem. 190, 243 (1962).

[0044] Accordingly, the compound of formula XIa is allowed to react with an ester of formula VIII in the presence of a base and an organic solvent such as benzene, toluene, alcohols such as methanol or ethanol, N,N-dimethylformamide or an ester, whereby the employed ester of formula VIII may itself serve as the solvent. Suitable bases for the above condensation reaction are for example sodium or potassium hydride, alcoholates such as sodium methylate or sodium ethylate, or potassium or sodium metal.

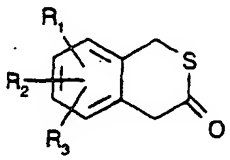
This reaction method is especially suitable for the production of compounds of formula VIIa, wherein m signifies 1.

[0045] For example, in the above manner, the new compound of formula $VIIa_1$



($VIIa_1$),

wherein R_1, R_2 and R_3 have the significances given under formula I, may be prepared from the compound of formula XIa_1



(XIa_1),

wherein R_1, R_2 and R_3 have the indicated significances.

[0046] The compounds of formula $VIIa_1$ are an important intermediate product for the synthesis of the compounds of formula I. The invention thus also relates to these compounds.

[0047] The starting compounds of formula VIIb may be produced e.g. analogously to WO 92/08703, Heterocycles 35, 305 (1993) or Z. Naturforsch. B, 34B, 283 (1979). The compound of formula XIb is accordingly allowed to react with the ortho-ester of formula IX in an excess of acetic acid anhydride (Ac_2O) for 2 to 24 hours at elevated temperatures, e.g. 100°C, to form the enol ether of formula VIIc. This may be cleaved under basic-aqueous conditions at temperatures of 0° to 25°C. Acidic-aqueous working up, for example in the presence of diluted mineral acids such as sulphuric or

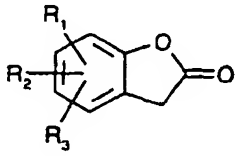
hydrochloric acid, yields the desired product of formula VIIb.

[0048] This method of reaction is especially suitable for the production of compounds of formula VIIb (m=0), wherein U has the significance given under formula I with the exception of $C(R_{15})R_{16}$, if R_{15} or R_{16} signifies hydrogen, or R_{15} and R_{16} are hydrogen simultaneously. For these derivatives, special processes are to be considered, e.g. those indicated in Tetrahedron Lett. 32, 851 (1991) or Chem. Ber. 107, 739 (1974).

[0049] The starting compounds of formulae VIII, IX, X, XIa and XIb are either known or may be produced according to disclosed processes.

[0050] For example, the production of the compound of formula XIa_1 is described in J. Heterocyclic Chem. 20, 811 (1983).

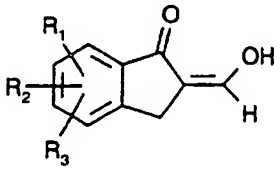
[0051] The production of the starting compound of formula XIb_1



(XIb_1)

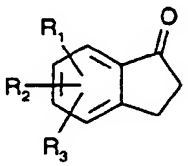
wherein R_1, R_2 and R_3 have the significances given under formula I, is described e.g. in FR-A-2 686 880.

[0052] The intermediate products of formula VIId



(VIId),

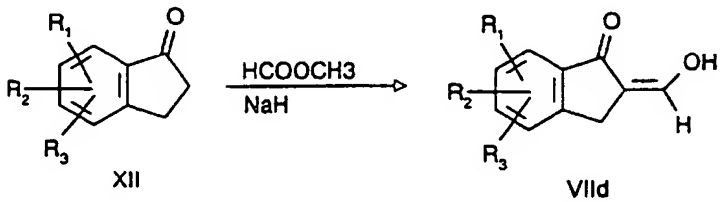
wherein R_1, R_2 and R_3 have the significances given under formula I, may be produced analogously to known processes, such as that described in J. Chem. Soc. 101, 2546 (1912), from the compounds of formula XII



(XII),

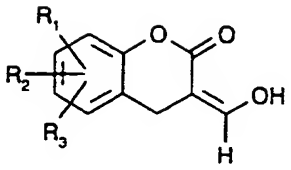
wherein R_1, R_2 and R_3 have the indicated significances, e.g. in accordance with the following reaction scheme 1.

Reaction scheme 1



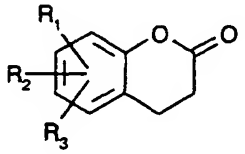
XII VIId

[0053] The intermediate products of formula VIIe



(VIIe),

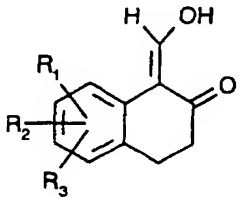
wherein R_1, R_2 and R_3 have the significances given under formula I, may be produced analogously to known processes, such as that described in Chem. Ber. 93, 1021 (1960), from the compounds of formula XIII



(XIII),

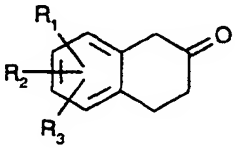
wherein R_1, R_2 and R_3 have the indicated significances.

[0054] The intermediate products of formula VIIf



(VIIf),

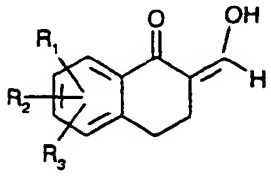
wherein R_1, R_2 and R_3 have the significances given under formula I, may be produced analogously to known processes, such as that described in Tetrahedron Lett. 1965, 1599, from the compounds of formula XIa_2



(XIa_2),

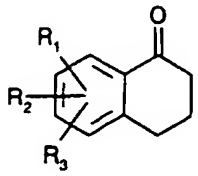
wherein R_1, R_2 and R_3 have the indicated significances.

[0055] The intermediate products of formula VIIg



(VIIg),

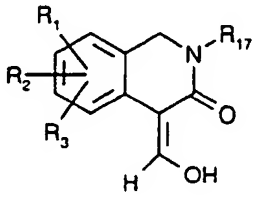
wherein R_1, R_2 and R_3 have the significances given under formula I, may be produced analogously to known processes, such as that described in J. Org. Chem. 15, 1135 (1950), from the compounds of formula XIVa



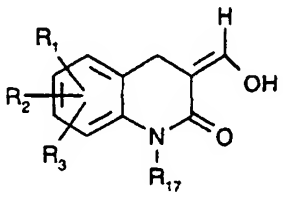
(XIVa),

wherein R_1, R_2 and R_3 have the indicated significances.

[0056] The intermediate products of formulae $VIIa_2$ and $VIIa_3$

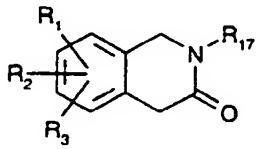


($VIIa_2$) and

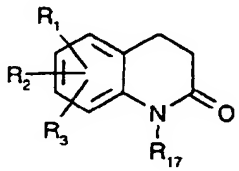


($VIIa_3$),

wherein R_1, R_2, R_3 and R_{17} have the significances given under formula I, may be produced from the compounds of formulae XIa_3 or XIa_4



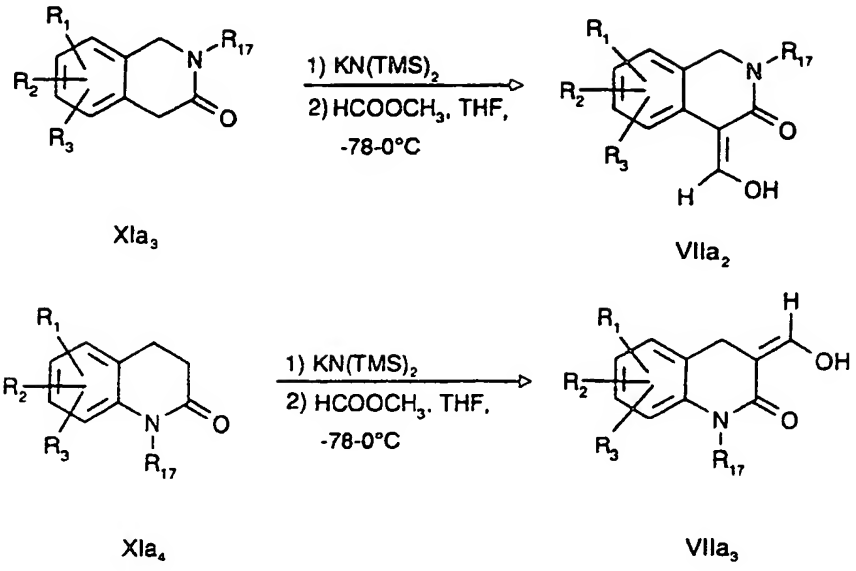
(XIa_3) or



(XIa_4),

wherein R_1, R_2, R_3 and R_{17} have the indicated significances, e.g. in accordance with the following reaction scheme 2.

Reaction scheme 2



XIa_3 $VIIa_2$

XIa_4 $VIIa_3$

[0057] The reaction of the compounds of formulae XIa_3 and XIa_4 with the formic acid ester according to reaction scheme 2 preferably takes place in an organic solvent such as ether, for example tetrahydrofuran (THF), at temperatures of -78°C to 0°C and in the presence of a base such as potassium-bis-(trimethylsilyl)-amide ($KN(TMS)_2$).

[0058] The compounds of formulae $VIIa_2$ and $VIIa_3$ are new and represent important intermediate products in the synthesis of the compounds of formula I. The invention thus also relates to these compounds.

[0059] The educts of formula XIa_3 in reaction scheme 2 may be obtained analogously to known processes, e.g. as described in Heterocyclic Chem. 32, 73 (1995).

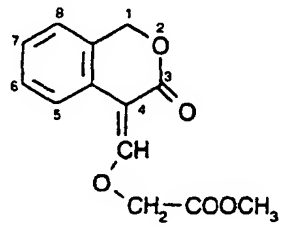
[0060] The educts of formula XIa_4 in reaction scheme 2 may be obtained analogously to known processes, e.g. as described in Synthesis 1987, 515.

[0061] The starting compounds of formulae XIa_2, XII, XIII and XIVa are either known or may be produced according to disclosed processes.

[0062] The following example further clarifies the invention without restricting it.

Preparation example H1: (3-oxo-isochroman-4-ylidenemethoxy)-acetic acid methyl ester

[0063]



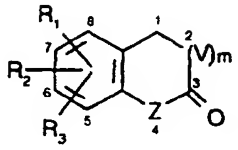
(Comp. No. 01.002)

4.48 g (0.025 mols) of 3H-2-benzopyran-3-one-1,4-dihydro-4-hydroxymethylene (Z. Anal. Chem. 190, 243 (1962)) in 10 ml of DMF are added dropwise over the course of 5 minutes at -5°C to a suspension of 1.2 g of sodium hydride (55% in oil) in 120 ml of DMF. Afterwards, 4.0 g (0.026 mols) of bromoacetic acid methyl ester are added. After removing

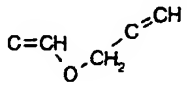
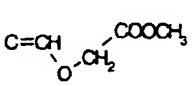
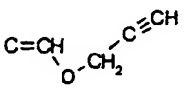
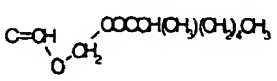
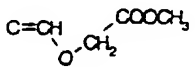
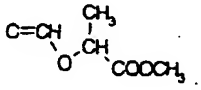
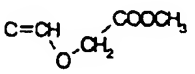
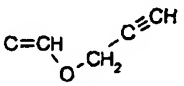
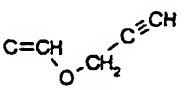
the cooling bath, stirring continues for 1¾ hours at 25°C. The reaction mixture is subsequently poured onto a mixture of 400 ml of ice water / 50 ml of 2N aqueous hydrochloric acid / 200 ml of ethyl acetate, the organic and aqueous phases are separated from one another and washed 3 times each with 100 ml of water and 100 ml of ethyl acetate. The combined organic phases are dried over sodium sulphate and concentrated. The oily residue obtained is triturated with diethylether/hexane and filtered. 5.34 g of the desired product are obtained with a m.p. of 81-82°C.

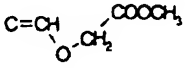
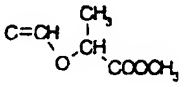
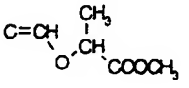
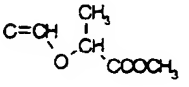
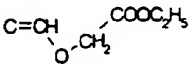
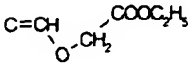
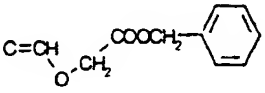
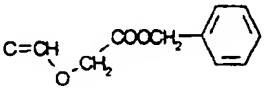
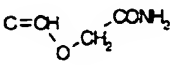
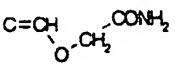
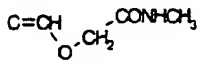
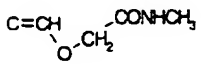
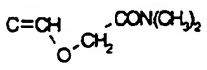
[0064] The compounds listed in the following tables may also be produced in analogous manner and according to methods illustrated in the documents cited.

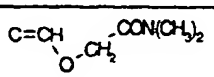
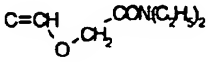
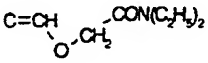
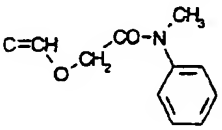
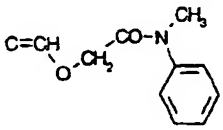
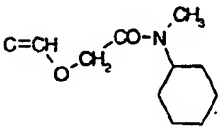
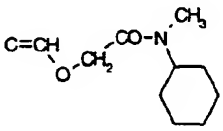
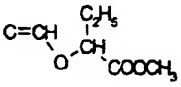
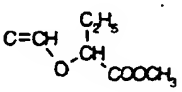
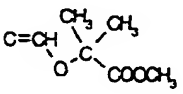
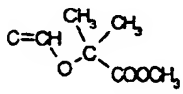
Table 01: Compounds of formula I_{01}

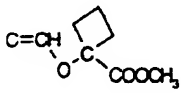
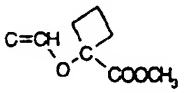
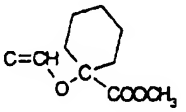
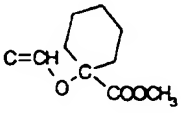
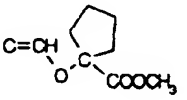
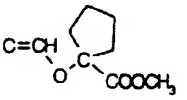
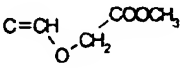
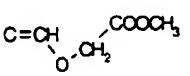
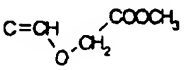
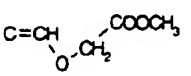
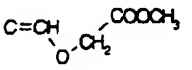


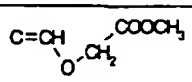
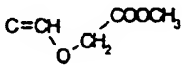
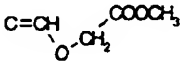
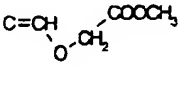
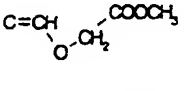
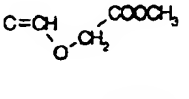
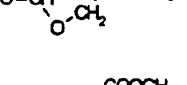
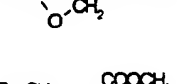
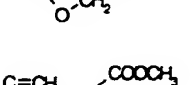
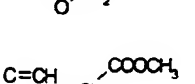
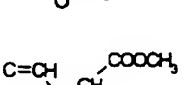
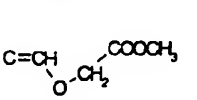
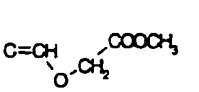
(I_{01})

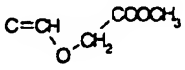
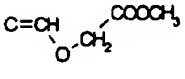
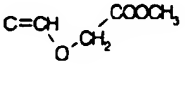
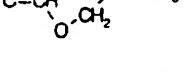
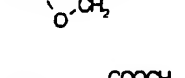
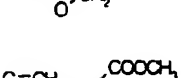
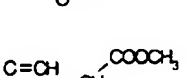
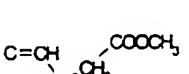
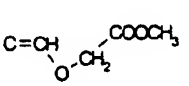
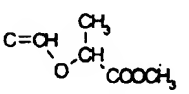
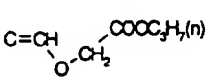
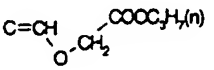
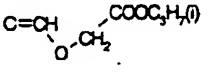
Comp. No.	R_1, R_2, R_3	Z	V	m	Phys.data m.p. [°C]
01.001	H, H, H		O	1	oil
01.002	H, H, H		O	1	81-82
01.003	H, H, H		O	1	83-86
01.004	H, H, H		O	1	44-46
01.005	H, H, H		CH_2	1	82-84
01.006	H, H, H		CH_2	1	70-72
01.007	H, H, H		S	1	94-95
01.008	H, H, H		S	1	75-76
01.009	H, H, H		NC H_3	1	solid

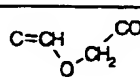
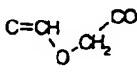
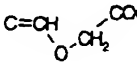
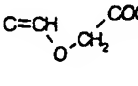
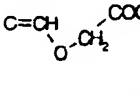
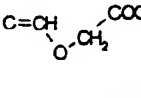
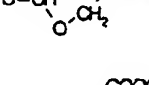
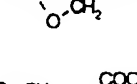
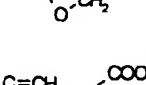
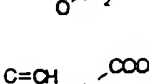
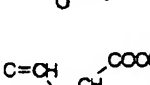
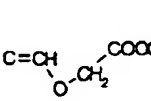
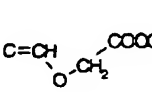
Comp. No.	R_1, R_2, R_3	Z	V	m	Phys.data m.p. [°C]
01.010	H, H, H		NCH$_3$	1	126-128
01.011	H, H, H		NCH$_3$	1	134-137
01.012	H, H, H		O	1	104-105
01.013	H, H, H		S	1	128-129
01.014	H, H, H		S	1	
01.015	H, H, H		O	1	
01.016	H, H, H		S	1	
01.017	H, H, H		O	1	
01.018	H, H, H		S	1	
01.019	H, H, H		O	1	
01.020	H, H, H		S	1	
01.021	H, H, H		O	1	
01.022	H, H, H		S	1	

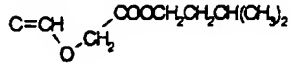
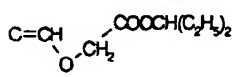
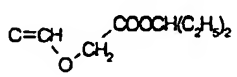
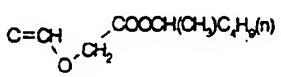
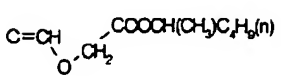
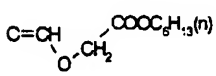
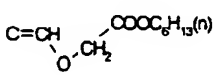
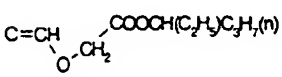
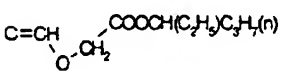
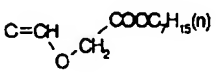
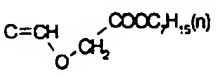
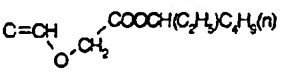
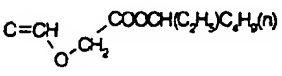
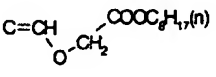
Comp. No.	R_1, R_2, R_3	Z	V	m	Phys.data m.p. [°C]
01.023	H, H, H		O	1	
01.024	H, H, H		S	1	
01.025	H, H, H		O	1	
01.026	H, H, H		S	1	
01.027	H, H, H		O	1	
01.028	H, H, H		S	1	
01.029	H, H, H		O	1	
01.030	H, H, H		S	1	
01.031	H, H, H		O	1	
01.032	H, H, H		S	1	
01.033	H, H, H		O	1	

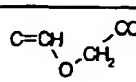
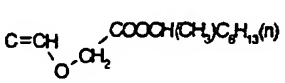
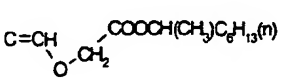
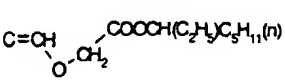
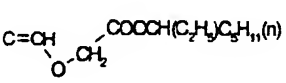
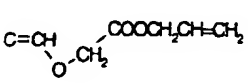
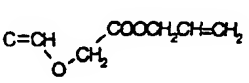
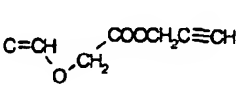
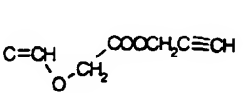
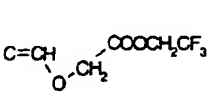
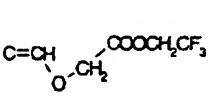
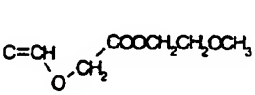
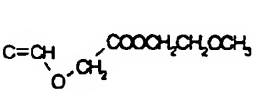
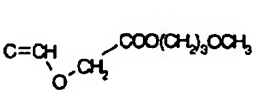
Comp. No.	R_1, R_2, R_3	Z	V	m	Phys.data m.p. [°C]
01.034	H, H, H		S	1	
01.035	H, H, H		O	1	
01.036	H, H, H		S	1	
01.037	H, H, H		O	1	
01.038	H, H, H		S	1	
01.039	H, H, H		O	1	
01.040	H, 7-CH_3, H		S	1	
01.041	H, 7-CH_3, H		O	1	
01.042	H, 6-CH_3, H		S	1	
01.043	H, 6-CH_3, H		O	1	
01.044	H, 7-OCH_3, H		S	1	

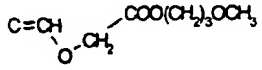
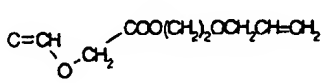
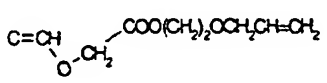
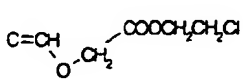
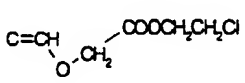
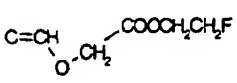
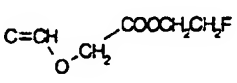
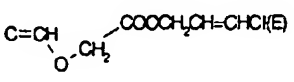
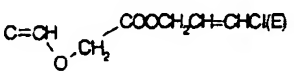
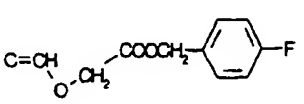
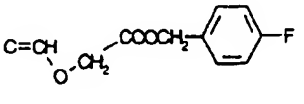
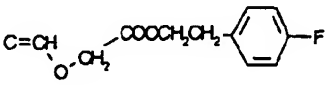
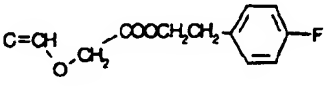
Comp. No.	R_1, R_2, R_3	Z	V	m	Phys.data m.p. [°C]
01.045	H, 7-OCH_3, H		O	1	
01.046	H, 7-Cl, H		S	1	
01.047	H, 7-Cl, H		O	1	
01.048	H, 6-Cl, H		S	1	
01.049	H, 6-Cl, H		O	1	
01.050	H, 8-CH_3, H		S	1	
01.051	H, 8-CH_3, H		O	1	
01.052	H, 5-CH_3, H		S	1	
01.053	H, 5-CH_3, H		O	1	
01.054	H, 8-Cl, H		S	1	
01.055	H, 8-Cl, H		O	1	
01.056	H, 5-Cl, H		S	1	
01.057	H, 5-Cl, H		O	1	
01.058	H, 6-OCH_3, H		S	1	

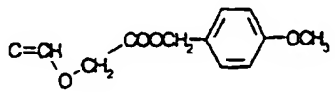
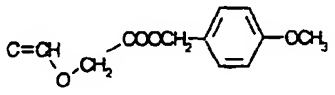
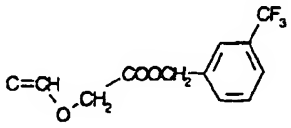
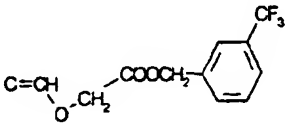
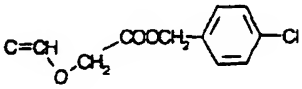
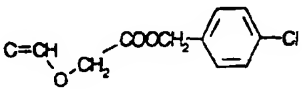
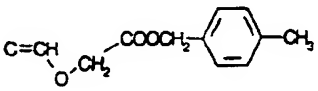
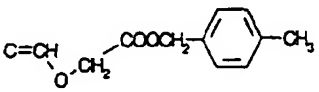
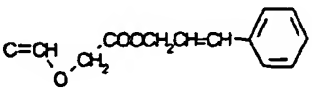
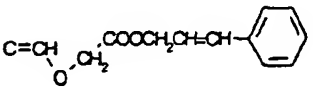
Comp. No.	R_1, R_2, R_3	Z	V	m	Phys.data m.p. [°C]
01.059	H, 6-OCH_3, H		O	1	
01.060	H, 8-OCH_3, H		S	1	
01.061	H, 8-OCH_3, H		O	1	
01.062	H, 5-OCH_3, H		S	1	
01.063	H, 5-OCH_3, H		O	1	
01.064	6-OCH_3,7-OCH_3, H		S	1	
01.065	6-OCH_3,7-OCH_3, H		O	1	
01.066	6-CH_3,7-CH_3, H		S	1	
01.067	6-CH_3,7-CH_3, H		O	1	
01.068	H, H, H		NH	1	
01.069	H, H, H		NH	1	
01.070	H, H, H		O	1	
01.071	H, H, H		S	1	
01.072	H, H, H		O	1	

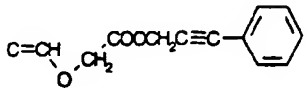
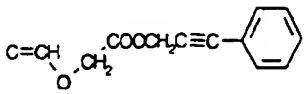
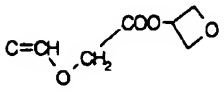
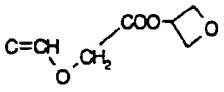
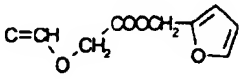
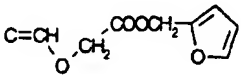
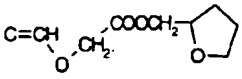
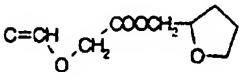
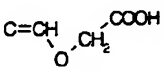
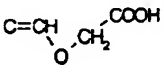
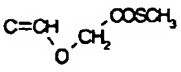
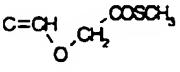
Comp. No.	R_1, R_2, R_3	Z	V	m	Phys.data m.p. [°C]
01.073	H, H, H		S	1	
01.074	H, H, H		O	1	
01.075	H, H, H		S	1	
01.076	H, H, H		O	1	
01.077	H, H, H		S	1	
01.078	H, H, H		O	1	
01.079	H, H, H		S	1	
01.080	H, H, H		O	1	
01.081	H, H, H		S	1	
01.082	H, H, H		O	1	
01.083	H, H, H		S	1	
01.084	H, H, H		O	1	
01.085	H, H, H		S	1	
01.086	H, H, H		O	1	

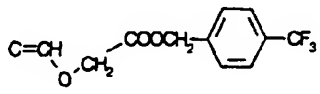
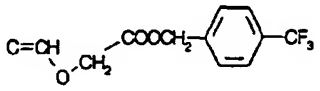
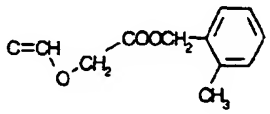
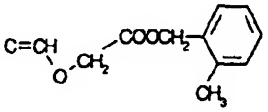
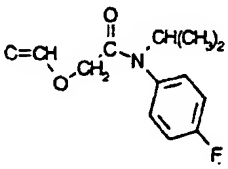
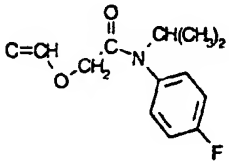
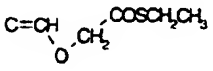
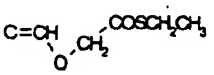
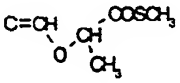
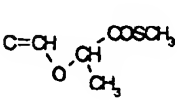
Comp. No.	R_1, R_2, R_3	Z	V	m	Phys.data m.p. [°C]
01.087	H, H, H		S	1	
01.088	H, H, H		O	1	
01.089	H, H, H		S	1	
01.090	H, H, H		O	1	
01.091	H, H, H		S	1	
01.092	H, H, H		O	1	
01.093	H, H, H		S	1	
01.094	H, H, H		O	1	
01.095	H, H, H		S	1	
01.096	H, H, H		O	1	
01.097	H, H, H		S	1	
01.098	H, H, H		O	1	
01.099	H, H, H		S	1	
01.100	H, H, H		O	1	

Comp. No.	R_1, R_2, R_3	Z	V	m	Phys.data m.p. [°C]
01.101	H, H, H		S	1	
01.102	H, H, H		O	1	
01.103	H, H, H		S	1	
01.104	H, H, H		O	1	
01.105	H, H, H		S	1	
01.106	H, H, H		O	1	
01.107	H, H, H		S	1	
01.108	H, H, H		O	1	
01-109	H, H, H		S	1	
01.110	H, H, H		O	1	
01.111	H, H, H		S	1	
01.112	H, H, H		O	1	
01.113	H, H, H		S	1	
01.114	H, H, H		O	1	

Comp. No.	R_1, R_2, R_3	Z	V	m	Phys.data m.p. [°C]
01.115	H, H, H		S	1	
01.116	H, H, H		O	1	
01.117	H, H, H		S	1	
01.118	H, H, H		O	1	
01.119	H, H, H		S	1	
01.120	H, H, H		O	1	
01.121	H, H, H		S	1	
01.122	H, H, H		O	1	
01.123	H, H, H		S	1	
01.124	H, H, H		O	1	
01.125	H, H, H		S	1	
01.126	H, H, H		O	1	
01.127	H, H, H		S	1	

Comp. No.	R_1, R_2, R_3	Z	V	m	Phys.data m.p. [°C]
01.128	H, H, H		O	1	
01.129	H, H, H		S	1	
01.130	H, H, H		O	1	
01.131	H, H, H		S	1	
01.132	H, H, H		O	1	
01.133	H, H, H		S	1	
01.134	H, H, H		O	1	
01.135	H, H, H		S	1	
01.136	H, H, H		O	1	
01.137	H, H, H		S	1	

Comp. No.	R_1, R_2, R_3	Z	V	m	Phys.data m.p. [°C]
01.138	H, H, H		O	1	
01.139	H, H, H		S	1	
01.140	H, H, H		O	1	
01.141	H, H, H		S	1	
01.142	H, H, H		O	1	
01.143	H, H, H		S	1	
01.144	H, H, H		O	1	
01.145	H, H, H		S	1	
01.146	H, H, H		O	1	
01.147	H, H, H		S	1	
01.148	H, H, H		O	1	
01.149	H, H, H		S	1	

Comp. No.	R_1, R_2, R_3	Z	V	m	Phys.data m.p. [°C]
01.150	H, H, H		O	1	
01.151	H, H, H		S	1	
01.152	H, H, H		O	1	
01.153	H, H, H		S	1	
01.154	H, H, H		O	1	
01.155	H, H, H		S	1	
01.156	H, H, H		O	1	
01.157	H, H, H		S	1	
01.158	H, H, H		O	1	
01.159	H, H, H		S	1	

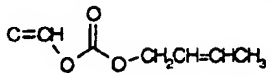
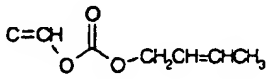
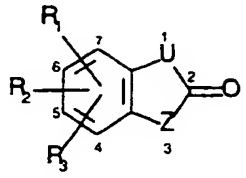
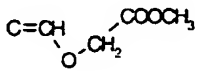
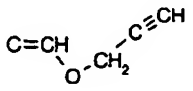
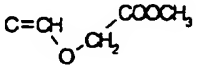
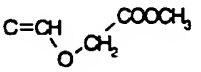
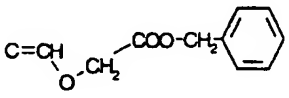
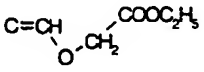
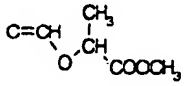
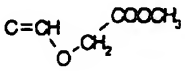
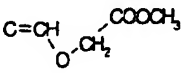
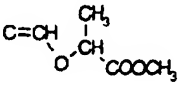
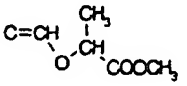
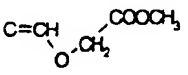
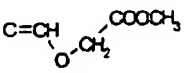
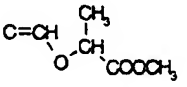
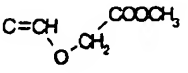
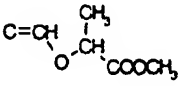
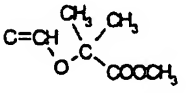
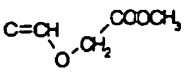
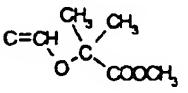
Comp. No.	R_1, R_2, R_3	Z	V	m	Phys.data m.p. [°C]
01.160	H, H, H		O	1	
01.161	H, H, H		S	1	

Table 02: Compounds of formula I_{02}



(I_{02})

Comp. No.	U	R_1, R_2, R_3	Z	Phys. data m.p. [°C]
02.001	O	H, H, H		114-117
02.002	O	H, H, H		108-117
02.003	O	H, 5-Cl, H		148-150
02.004	CH_2	H, H, H		113-117
02.005	CH_2	H, H, H		114-116
02.006	CH_2	H, H, H		83-85

Comp. No.	U	R_1, R_2, R_3	Z	Phys. data m.p. [°C]
02.007	NH	H, 5-Cl, H		196-197
02.008	NH	H, 5-Cl, H		157-159
02.009	NH	H, H, H		169-171
02.010	NH	H, H, H		resin
02.011	NCH_3	H, H, H		146-147
02.012	NCH_3	H, H, H		111-112
02.013	S	H, H, H		
02.014	S	H, H, H		
02.015	CH_2	H, 6-Cl, H		
02.016	CH_2	H, 6-Cl, H		
02.017	CH_2	H, 6-Cl, H		
02.018	CH_2	H, 6-OCH_3, H		
02.019	CH_2	H, 6-OCH_3, H		

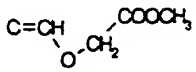
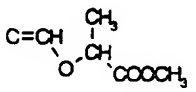
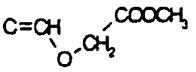
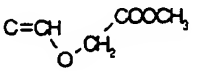
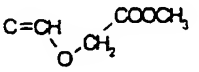
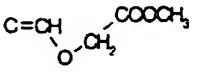
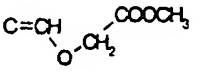
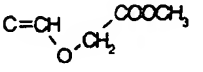
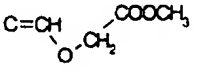
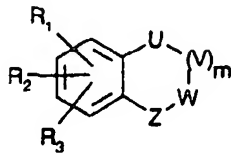
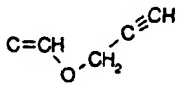
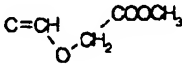
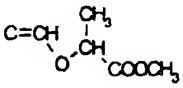
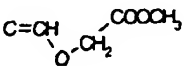
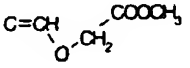
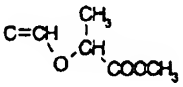
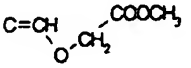
Comp. No.	U	R_1, R_2, R_3	Z	Phys. data m.p. [°C]
02.020	CH_2	6-CH_3, H, H		
02.021	CH_2	6-CH_3, H, H		
02.022	CH_2	H, 5-Cl, H		
02.023	CH_2	5-OCH_3, H, H		
02.024	CH_2	5-CH_3, H, H		
02.025	CH_2	5-OCH_3, 6-OCH_3, H		
02.026	CH_2	5-CH_3, 6-CH_3, H		
02.027	CH_2	7-CH_3, H, H		
02.028	CH_2	4-CH_3, H, H		

Table 03: Compounds of formula I_{03}



(I_{03})

Comp. No.	U	V	m	W	Z	R_1, R_2, R_3	Phys. data m.p. [°C]
03.001	O	C=O	1		CH_2	H, H, H	waxy
03.002	O	C=O	1		CH_2	H, H, H	71-73
03.003	CH_2	C=O	1		CH_2	H, H, H	123-125
03.004	CH_2	C=O	1		CH_2	H, H, H	98-100
03.005	CH_2	CH_2	1		C=O	H, H, H	97-98
03.006	CH_2	CH_2	1		C=O	H, H, H	55-58
03.007	NCH_3	C=O	1		CH_2	H, H, H	waxy

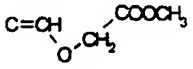
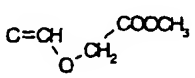
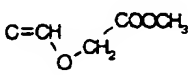
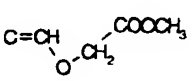
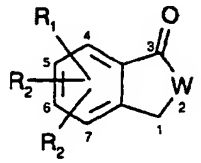
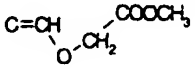
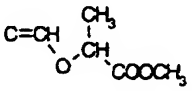
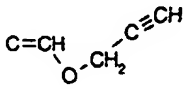
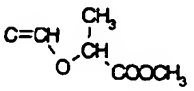
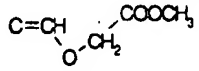
Comp. No.	U	V	m	W	Z	R_1, R_2, R_3	Phys. data m.p. [°C]
03.008	$CHCH_3$	O	1	C=O		H, H, H	
03.009	$CHCH_3$	S	1	C=O		H, H, H	
03.010	$C(CH_3)_2$	O	1	C=O		H, H, H	
03.011	$C(CH_3)_2$	S	1	C=O		H, H, H	

Table 04: Compounds of formula I_{04}



(I_{04})

Comp. No.	R_1, R_2, R_3	W	Phys. data m.p. [°C]
04.001	H, 6-Cl, H		144-146
04.002	H, 6-Cl, H		98-100
04.003	H, H, H		119-121
04.004	H, H, H		104-106

Comp. No.	R_1, R_2, R_3 W	Phys. data m.p. [°C]
04.005	H, H, H 	114-116

[0065] The compounds of formula I according to the invention may be used as antidotes in herbicidal compositions.

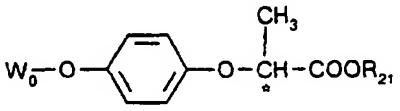
[0066] When using herbicides, the cultivated plants may also be damaged to a considerable extent e.g. depending on the dosage of herbicide and the type of application, the plant being cultivated, the constitution of the soil and the climatic conditions, such as duration of light, temperature and amount of rainfall.

[0067] In order to counteract this and similar problems, already many substances have been proposed as antidotes. These are capable of antagonizing the damaging activity of the herbicide on the cultivated plant, that is, protecting the cultivated plant therefrom, whereby however the herbicide activity on the weeds to be controlled is practically unimpaired. As a result, it has been shown that the proposed antidotes often have very specific activity both in regard of the cultivated plants and in regard of the herbicide and partly also depending on the type of application. This means that a certain antidote is often only suitable for a certain cultivated plant and a particular class of herbicide substance or a certain herbicide.

[0068] It has now been found that the compounds of formula I according to the invention are suitable for protecting cultivated plants from the phytotoxic activity of certain classes of aryloxy-phenoxypropionic acid ester, sulphonylurea, sulphonamide, 3-hydroxy-4-aryl-5-oxo-pyrazoline and chloracetanilide herbicides and the herbicide isoxaflutol (EXP-30953).

[0069] Thus, in accordance with the invention, a herbicidal composition having selective herbicide activity is also proposed, which is characterised in that, in addition to the usual inert formulation assistants such as carriers, solvents and wetting agents, it contains as the active ingredient a mixture of

a) a herbicidally active amount of a herbicide of formulae II to VII

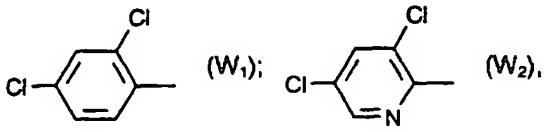


(II),

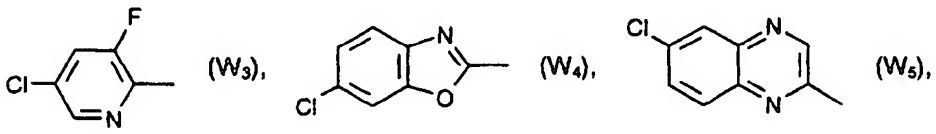
wherein

R_{21} signifies C_1-C_4-alkyl, propargyl or the group $-CH_2-CH_2-O-N=C(CH_3)_2$; and

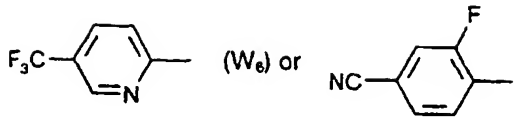
W_o signifies the groups



(W_1); (W_2),

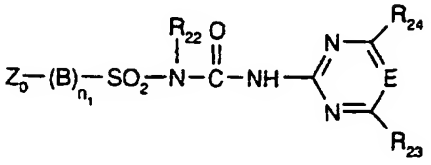


(W_3), (W_4), (W_5),

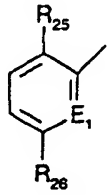
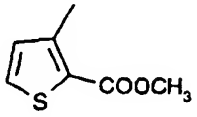

(W6) or

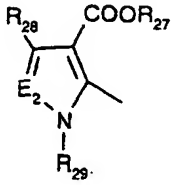
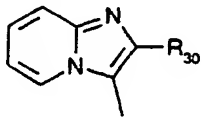
(W7) ,

and in particular the
(R)-enantiomers (*) of these compounds; or of formula III

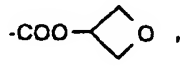

(III),

wherein Z_o signifies a group

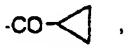

(Z1),

(Z2),


(Z3),

(Z4) or CH_3-SO_2- (Z5);

R_{22} signifies hydrogen or CH_3;
R_{23} signifies CH_3, -OCH_3, -$OCHF_2$, Cl, -$N(CH_3)_2$, -$NHCH_3$ or CF_3;
R_{24} signifies CH_3, -OCH_3, -$OCHF_2$, -OCH_2CF_3 or -OC_2H_5;
R_{25} signifies -OC_2H_5, -OCH_2CH_2Cl, -$COOCH_3$, -$COOC_2H_5$,

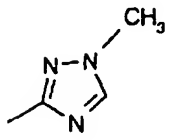

,

-O-CH_2CH_2-O-CH_3, Cl, -$CON(CH_3)_2$, -$SO_2C_2H_5$, CF_3, -$OCHF_2$,


,

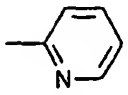
-$N(CH_3)SO_2CH_3$ or -$N(CH_3)COCH_3$;

R_{26} signifies hydrogen, CH_3, $-OCH_3$, CF_3, CHF_2 or $-OCHF_2$;
R_{27} signifies CH_3, C_2H_5 or the group



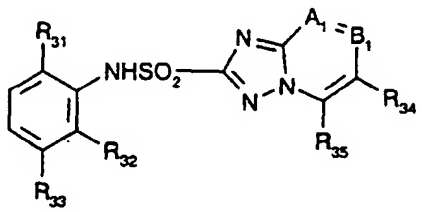
;

R_{28} signifies hydrogen or chlorine;
R_{29} signifies CH_3 or the group



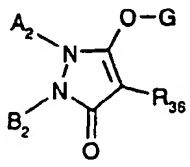
;

R_{30} signifies $-SO_2C_2H_5$ or chlorine;
E signifies nitrogen or methine;
E_1 signifies nitrogen, methine or C-CH_3;
E_2 signifies nitrogen or methine;
B signifies oxygen, -NH- or methylene; and
n_1 signifies 0 or 1, as well as agronomically compatible salts of these compounds; or of formula IV



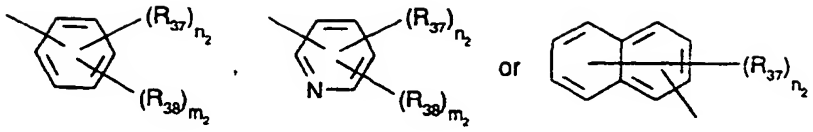
(IV),

wherein
R_{31} is fluorine or chlorine;
R_{32} is fluorine, chlorine or $-COOCH_3$;
R_{33} is hydrogen or methyl;
R_{34} is hydrogen or fluorine;
R_{35} is hydrogen or methoxy;
A_1 is nitrogen or C-OC_2H_5; and
B_1 is nitrogen, C-CH_3 or C-OCH_3; or of formula V

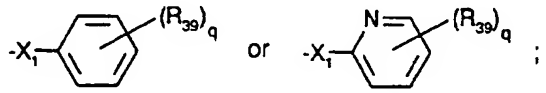


(V),

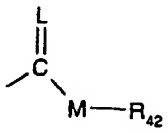
wherein
R_{36} signifies the group



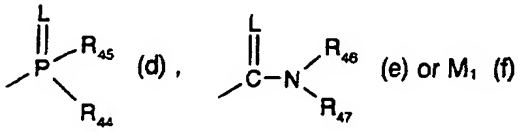
the substituents R_{37}, independently of one another, signify halogen, nitro, cyano, C_1-C_4-alkyl, C_1-C_4-halogen-alkyl, C_1-C_{10}-alkoxy, C_1-C_4-halogen-alkoxy, C_3-C_6-alkenyloxy, C_1-C_4-alkoxy-C_2-C_4-alkoxy, C_3-C_6-alkinyloxy, C_1-C_4-alkylcarbonyl, C_1-C_4-alkoxycarbonyl, C_1-C_4-alkylthio, C_1-C_4-alkylsulphinyl, C_1-C_4-alkylsulphonyl, amino, C_1-C_4-alkylamino or di-C_1-C_4-alkylamino;
R_{38} signifies the group



n_2 signifies 0, 1, 2, 3 or 4;
m_2 signifies 0 or 1, whereby the sum of m_2 and n_2 is 0, 1, 2, 3 or 4;
q signifies 0, 1, 2 or 3;
X_1 is oxygen, sulphur, $-CH_2-$ or $-N(R_{40})-$;
the substituents R_{39}, independently of one another, are C_1-C_4-alkyl, halogen, C_1-C_4-halogen-alkyl, C_1-C_4-alkoxy, C_1-C_4-halogen-alkoxy, nitro, cyano, C_1-C_4-alkoxycarbonyl, amino, C_1-C_4-alkylamino or di-C_1-C_4-alkylamino;
R_{40} signifies hydrogen, C_1-C_4-alkyl, formyl or C_1-C_4-alkylcarbonyl;
A_2 and B_2, independently of one another, signify hydrogen, alkyl, alkenyl, alkinyl, alkoxyalkyl, alkylthioalkyl or cycloalkyl, or optionally substituted aryl; or
A_2 and B_2 together form the bivalent radical of a saturated or unsaturated and optionally substituted mono-, bi-, tri- or polycyclic system;
G signifies hydrogen or the groups $-CO-R_{41}$ (a),

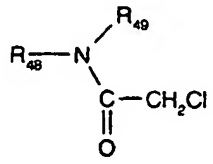


(b), $-SO_2-R_{43}$ (c),



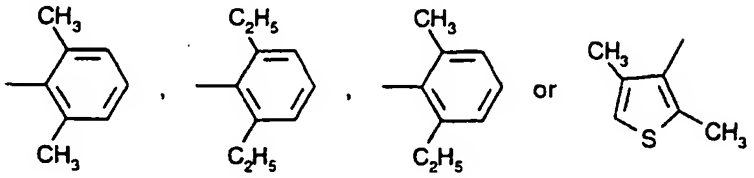
L and M, independently of one another, are oxygen or sulphur;
R_{41} is halogen-alkyl, alkenyl, alkoxyalkyl, alkylthioalkyl, polyalkoxyalkyl or cycloalkyl, which may contain hetero atoms, optionally substituted phenyl, optionally substituted phenylalkyl, substituted heteroaryl, substituted phenoxyalkyl or substituted heteroaryloxyalkyl;
R_{42} is halogen-alkyl, alkenyl, alkoxyalkyl or polyalkoxyalkyl, or optionally substituted phenyl or benzyl;
R_{43}, R_{44} and R_{45}, independently of one another, are alkyl, halogen-alkyl, alkoxy, alkylamino, dialkylamino, alkylthio, alkenylthio, alkinylthio or cycloalkylthio, or optionally substituted phenyl, phenoxy or phenylthio;
R_{46} and R_{47}, independently of one another, are hydrogen, alkyl, halogen-alkyl, alkenyl, alkoxy or alkoxyalkyl, optionally substituted phenyl or benzyl; or
R_{46} and R_{47} together form an alkylene radical, which may optionally contain oxygen as a hetero atom; and

M_1 signifies a metal ion equivalent or an ammonium ion,
as well as salts and diastereoisomers of the compounds of formula V; or of formula VI

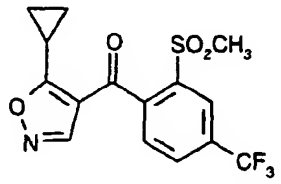


(VI),

wherein R_{48} signifies a group

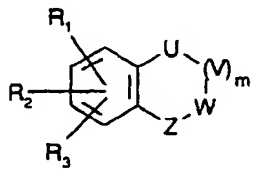


; and
R_{49} signifies a group $-CH(CH_3)CH_2OCH_3$, $-CH_2OCH_3$ or $-CH_2OC_2H_5$; or of formula VII



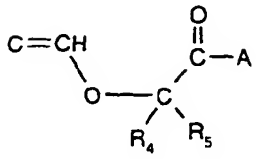
(VII, Isoxaflutol EXP-30953); and

b) an amount of an antidote of formula I



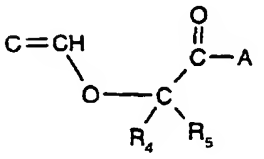
(I),

having herbicide-antagonistic activity, wherein
R_1 is hydrogen, C_1-C_4-alkyl, C_1-C_4-alkyl substituted by C_1-C_4-alkyl-X- or C_1-C_4-halogen-alkyl-X-, C_1-C_4-halogen-alkyl, nitro, cyano, $-COOR_8$, $-NR_9R_{10}$, $-SO_2NR_{11}R_{12}$ or $-CONR_{13}R_{14}$;
R_2 is hydrogen, halogen, C_1-C_4-alkyl, trifluoromethyl, C_1-C_4-alkoxy or C_1-C_4-halogen-alkoxy;
R_3 is hydrogen, halogen or C_1-C_4-Alkyl;
U, V, W and Z independently of one another, are oxygen, sulphur, $C(R_{15})R_{16}$, carbonyl, NR_{17} or a group



with the provisos that

a) at least one of the ring members U, V, W or Z is carbonyl, and a ring member which is adjacent to this or these ring members signifies the group



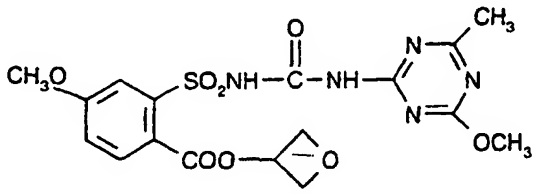
whereby this group only appears once; and

b) two adjacent ring members U and V, V and W and W and Z may not simultaneously signify oxygen;
R_4 and R_5, independently of one another, signify hydrogen or C_1-C_8-alkyl; or
R_4 and R_5 together form a C_2-C_6-alkylene group;
A is R_7-Y- or -$NR_{18}R_{19}$;
X is oxygen or -$S(O)_p$;
Y is oxygen or sulphur;
R_7 is hydrogen, C_1-C_8-alkyl, C_1-C_8-halogen-alkyl, C_1-C_4-alkoxy-C_1-C_8-alkyl, C_3-C_6-alkenyloxy-C_1-C_8-alkyl or phenyl-C_1-C_8-alkyl, whereby the phenyl ring may be substituted by halogen, C_1-C_4-alkyl, trifluormethyl, methoxy or methyl-$S(O)_p$-; C_3-C_6-alkenyl, C_3-C_6-halogen-alkenyl, phenyl-C_3-C_6-alkenyl, C_3-C_6-alkinyl, phenyl-C_3-C_6-alkinyl, oxetanyl, furfuryl or tetrahydrofurfuryl;
R_8 is hydrogen or C_1-C_4-alkyl;
R_9 is hydrogen, C_1-C_4-alkyl or C_1-C_4-alkylcarbonyl;
R_{10} is hydrogen or C_1-C_4-alkyl; or
R_9 and R_{10} together form a C_4- or C_5-alkylene group;
R_{11}, R_{12}, R_{13} and R_{14} independently of one another, are hydrogen or C_1-C_4-alkyl; or R_{11} together with R_{12} or R_{13} together with R_{14} independently of one another, are C_4- or C_5-alkylene, whereby one carbon atom may be replaced by oxygen or sulphur, or one or two carbon atoms may be replaced by -NR_{15}-;
R_{15} and R_{16} independently of one another, are hydrogen or C_1-C_8-alkyl; or
R_{15} and R_{16} together are C_2-C_6-alkylene;
R_{17} is hydrogen, C_1-C_8-alkyl, optionally substituted phenyl or benzyl optionally substituted on the phenyl ring;
R_{18} is hydrogen, C_1-C_8-alkyl, phenyl, phenyl-C_1-C_8-alkyl, whereby the phenyl ring may be substituted by fluorine, chlorine, bromine, nitro, cyano, -OCH_3, C_1-C_4-alkyl or CH_3SO_2-; C_1-C_4-alkoxy-C_1-C_8-alkyl, C_3-C_6-alkenyl, C_3-C_6-alkinyl or C_3-C_6-cycloalkyl;
R_{19} is hydrogen, C_1-C_8-alkyl, C_3-C_6-alkenyl or C_3-C_6-alkinyl; or
R_{18} and R_{19} together are C_4- or C_5-alkylene, whereby one carbon atom may be replaced by oxygen or sulphur, or one or two carbon atoms may be replaced by -NR_{20}-;
R_{20} is hydrogen or C_1-C_4-alkyl;
m is 0 or 1; and
p signifies 0, 1 or 2,
as well as agronomically compatible salts and stereoisomers of these compounds.

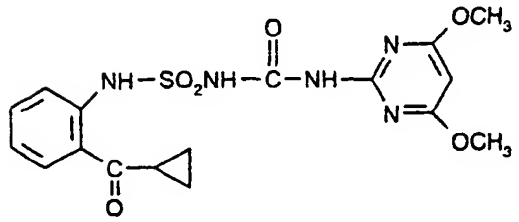
[0070] Preferred compositions according to the present invention contain clodinafop, quizalafop, propaquizafop, fenoxaprop, fluazifop and cyhalofop as the herbicides of formula II.

[0071] Preferred compositions according to the present invention contain tribenuron, metsulfuron, primisulfuron, ethametsulfuron, sulfometuron, chlorimuron, oxasulfuron [presented on the occasion of the Brighton Crop Protection

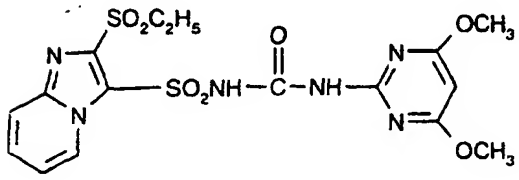
Conference - Weeds - 1995 (Plenary Session 2, November 21, 1995, Proceedings Vol. 2, page 79)], triasulfuron, cinosulfuron, triflusulfuron, bensulfuron, ethoxysulfuron, sulfazuron, nicosulfuron, rimsulfuron, flupyrsulfuron, thifensulfuron, clopyrazosulfuron (NC-319), pyrazosulfuron (NC-311), sulfosulfuron (NC-330, known from US-A-4 895 590), azimsulfuron und amidosulfuron as the herbicides of formula III, as well as the compounds of formulae IIIa to IIId



(IIIa) , known from EP-B-0 496 701;

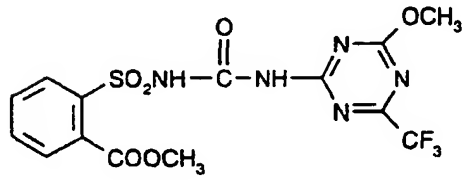


(IIIb), known from US-A-5 009 699;



(IIIc; MON-37500), known from

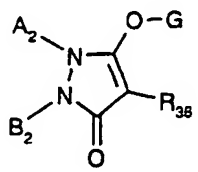
[0072] EP-A-0 477 808, and



(IIId), known from DE-OS-4 128 441,

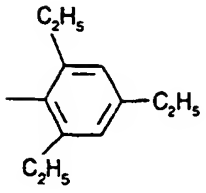
[0073] Preferred compositions according to the present invention contain flumetsulam, metosulam und cloransulam as herbicides of formula IV.

[0074] Preferred compositions according to the present invention contain the herbicides of formula V



(V),

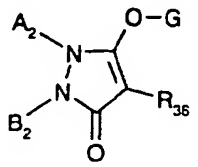
wherein R_{36} is mesitylenyl or



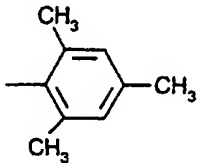
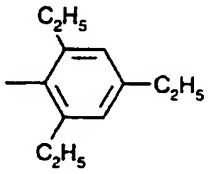
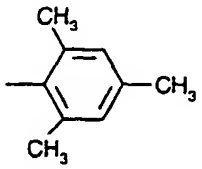
A_2 and B_2 are methyl; or A_2 and B_2 together form a $-(CH_2)_4-$ group; and G signifies hydrogen or $-COC(CH_3)_3$.

[0075] Of these, the herbicides of formula V according to table 1 are preferred in particular.

Table 1: Especially preferred herbicides of formula V



(V)

Comp. No.	A_2	B_2	R_{36}	G
1.1	$-(CH_2)_4-$			H
1.2	$-(CH_2)_4-$			H
1.3	CH_3	CH_3		$-C(O)C(CH_3)_3$

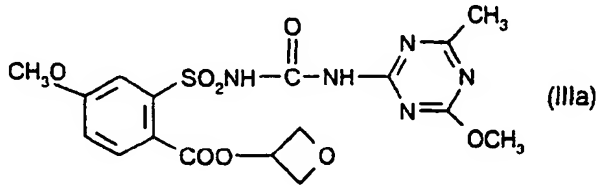
[0076] Preferred compositions according to the present invention contain metolachlor, alachlor, acetochlor, dimethenamide and in particular aRS,1'S(-)N-(1'-methyl-2'-methoxyethyl)-N-chloracetyl-2-ethyl-6-methylaniline, known from US-A-5 002 606, as herbicides of formula VI.

[0077] The compounds described by common names e.g. under formula II, such as clodinafop, under formula III

such as primisulfuron, under formula IV such as flumetsulam, under formula VI such as metolachlor and under formula VII (isoxaflutol) are known in part as commercial products or may be referred to for example in current agrochemical handbooks, e.g. 'The Pesticide Manual', The British Crop Protection Council, London; or 'The Agrochemicals Handbook', The Royal Society of Chemistry.

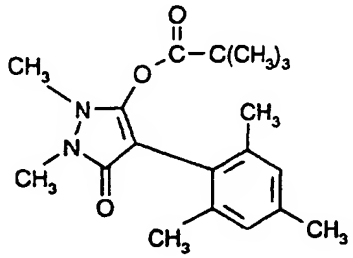
[0078] The compounds of formula V are known from international patent application No. WO-A-9611574 (PCT/EP 95/03935).

[0079] Preferred compositions according to the present invention are characterised in that they contain as the compound of formula I (3-oxo-isochroman-4-ylidenemethoxy)-acetic acid methyl ester (compound no. 01.002) in combination with clodinafop, primisulfuron, chlorimuron or in combination with the compound of formula



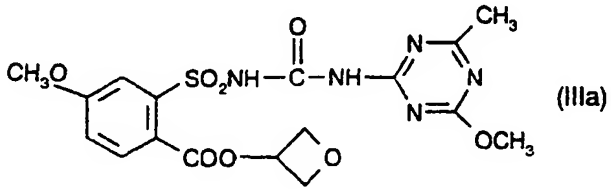
(IIIa)

or



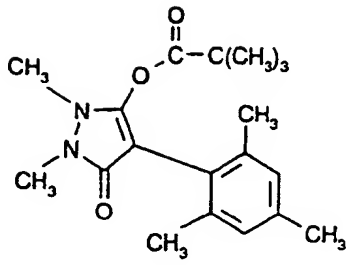
(Comp. No. 1.3).

[0080] Equally preferred compositions according to the present invention are characterised in that they contain as the compound of formula I (2-oxo-indan-1-ylidenemethoxy)-acetic acid methyl ester (compound no. 02.004) in combination with clodinafop, primisulfuron, chlorimuron or in combination with the compound of formula



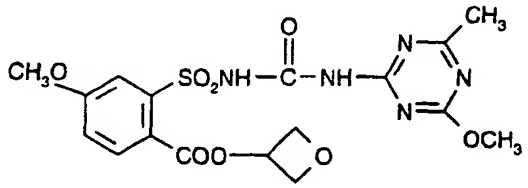
(IIIa)

or



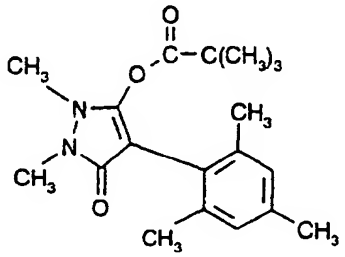
(Comp. no. 1.3).

[0081] Compositions according to the present invention which are also preferred are characterised in that they contain as the compound of formula I (3-oxo-isochrom-4-ylidenemethoxy)-acetic acid methyl ester (comp. no. 01.002), (2-oxo-indan-1-ylidenemethoxy)- acetic acid methyl ester (comp. no. 02.004) or (3-oxo-isothiochroman-4-ylidenemethoxy)-acetic acid methyl ester (comp. no. 01.007) and as the active ingredient of formula II clodinafop, as active ingredients of formula III primisulfuron, chlorimuron or the compound of formula



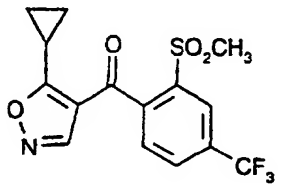
(IIIa),

as active ingredient of formula V the compound of formula



(Comp. No. 1.3)

and as active ingredient the compound of formula VII



(VII).

The invention also relates to a process for the selective control of weeds in useful plant cultivations, which comprises treating the useful plants, their seeds or cuttings or their cultivation area simultaneously or separately with a herbicidally active amount of a herbicide of formulae II to VI and a herbicide-antagonistically active amount of the antidote of formula I.

[0082] The cultivated plants that may be protected by the antidotes of formula I against the damaging action of the above-mentioned herbicides are in particular maize, cereals, soybeans and rice. The cultivations are understood to be also those which have been made tolerant towards herbicides or classes of herbicide by conventional growing methods or genetic engineering methods.

[0083] The weeds to be controlled may be both monocotyledonous and dicotyledonous weeds, for example *Stellaria, Nasturtium, Agrostis, Digitaria, Avena, Setaria, Sinapis, Lolium, Solanum, Phaseolus, Echinochloa, Scirpus, Monochoria, Sagittaria, Bromus, Alopecurus, Sorghum halepense, Rottboellia, Cyperus, Abutilon, Sida, Xanthium, Amaranthus, Chenopodium, Ipomoea, Chrysanthemum, Galium, Viola* and *Veronica*.

[0084] The cultivation areas include the soil on which the cultivated plants are already growing or on which seed of these cultivated plants has already been sown, and also the soil on which these cultivated plants are intended to be raised.

[0085] Depending on the purpose of application, an antidote of formula I may be employed for the pre-treatment of the seed grain of the culvitated plant (dressing of the seed or cuttings) or may be added to the soil before or after sowing. However, it may also be applied on its own or together with the herbicide after emergence of the plants. Therefore, treatment of the plants or the seed grain with the antidote may basically take place independently of the time of application of the herbicide. However, treatment of the plant may also be undertaken by means of simultaneous application of herbicide and antidote (e.g. as a tank mixture).

[0086] The application rate of antidote to herbicide to be employed depends to a great extent on the type of application. For field treatment, which is effected either using a tank mixture with a combination of antidote and herbicide or by means of separate application of antidote and herbicide, a ratio of herbicide to antidote of 1:100 to 100:1, preferably 1:20 to 20:1 is normal.

[0087] As a rule, for field treatment, 0.001 to 5.0 kg antidote/ha, preferably 0.001 to 0.5 kg antidote/ha is applied.

[0088] The amounts of herbicide applied are usually between 0.001 and 2 kg/ha, but preferably between 0.005 and 1 kg/ha.

[0089] The compositions according to the invention are suitable for all application methods that are customary in agriculture, such as pre-emergent application, post-emergent application and seed dressing.

[0090] For seed dressing, in general 0.001 to 10 g of antidote/kg seeds, preferably 0.05 to 2 g antidote/kg seeds is applied. If the antidote is applied in liquid form shortly prior to sowing whereby the seed swells, antidote solutions which contain the active ingredient in a concentration of 1 to 10,000, preferably 100 to 1000 ppm are suitably used.

[0091] In order to apply them, the antidotes of formula I or combinations of these antidotes with the herbicides of formulae II to VI are conveniently processed with the assistants which are customary in formulation technology into formulations, e.g. into emulsion concentrates, coatable pastes, directly sprayable or dilutable solutions, diluted emulsions, wettable powders, soluble powders, dusts, granulates or micro-capsules. The formulations are produced in a manner known *per se*, e.g. by intimately mixing and/or grinding the active ingredients with liquid or solid formulating assistants such as solvents or solid carriers. In addition, surface-active compounds (surfactants) may be used when producing the formulations.

[0092] The solvents in question may be: aromatic hydrocarbons, preferably fractions C_8 to C_{12}, such as xylene mixtures or substituted naphthalenes, phthalic acid esters such as dibutyl or dioctyl phthalate, aliphatic hydrocarbons such as cyclohexane or paraffins, alcohols and glycols, as well as the ethers and esters thereof, such as ethanol, ethylene glycol, ethylene glycol monomethyl- or -ethyl-ether, ketones such as cyclohexanone, strongly polar solvents such as N-methyl-2-pyrrolidone, dimethyl sulphoxide or N,N-dimethylformamide, as well as optionally epoxidated vegetable oils such as epoxidated coconut oil or soybean oil; or water.

[0093] The solid carriers employed e.g. for dusts and dispersible powders are normally natural mineral powders, such as calcite, talc, kaolin, montmorillonite or attapulgite. To improve the physical properties of the formulation, highly disperse silicic acid or highly disperse absorbent polymerisates may also be added. The granular, adsorptive granulate carriers employed may be porous types such as pumice, brick fragments, sepiolite or bentonite, and the non-absorbent carrier materials are e.g. calcite or sand. Moreover, a number of pregranulated materials of inorganic or organic nature may also be used, especially dolomite or pulverized plant residue.

[0094] Depending on the type of active ingredients of formulae II to VI to be formulated, the surface-active compounds may be non-ionic, cationic and/or anionic surfactants and surfactant mixtures having good emulsifying, dispersing and wetting properties.

[0095] Appropriate anionic surfactants may be both so-called water-soluble soaps and water-soluble synthetic surface-active compounds.

[0096] Soaps which may be mentioned are the alkali salts, alkaline earth salts or optionally substituted ammonium salts of higher fatty acids (C_{10}-C_{22}), e.g. the Na or K salts of oleic or stearic acid, or of natural fatty acid mixtures, which may be obtained e.g. from coconut oil or tallow oil. Furthermore, the fatty acid methyl-taurine salts may also be mentioned.

[0097] More frequently however, so-called synthetic surfactants are used, especially fatty alcohol sulphonates, fatty

alcohol sulphates, sulphonated benzimidazole derivatives or alkylaryl sulphonates.

[0098] The fatty alcohol sulphonates or sulphates are normally present as alkali salts, alkaline earth salts or optionally substituted ammonium salts and have an alkyl radical with 8 to 22 C-atoms, whereby alkyl also includes the alkyl moiety of acyl radicals, e.g. the Na or Ca salt of lignin sulphonic acid, of dodecylsulphuric acid ester or of a fatty alcohol sulphate mixture produced from natural fatty acids. This also includes the salts of sulphuric acid esters and sulphonic acids of fatty alcohol/ethylene oxide adducts. The sulphonated benzimidazole derivatives preferably contain 2 sulphonic acid groups and one fatty acid radical with 8-22 carbon atoms. Alkylaryl sulphonates are e.g. the Na, Ca or triethanolamine salts of dodecylbenzenesulphonic acid, of dibutylnaphthalene-sulphonic acid or of a naphthalene-sulphonic acid / formaldehyde condensation product.

[0099] The corresponding phosphates such as the salts of the phosphoric acid ester of a p-nonyl-phenol-(4-14)-ethylene oxide adduct or phospholipids may also be considered.

[0100] The non-ionic surfactants may be primarily polyglycol ether derivatives of aliphatic or cycloaliphatic alcohols, saturated or unsaturated fatty acids and alkylphenols, which may contain 3 to 30 glycol ether groups and 8 to 20 carbon atoms in the (aliphatic) hydrocarbon radical and 6 to 18 carbon atoms in the alkyl radical of the alkylphenols.

[0101] Further appropriate non-ionic surfactants are the water-soluble polyethylene oxide adducts to polypropylene glycol, ethylenediamino-polypropylene glycol and alkyl-polypropylene glycol, containing 20 to 250 ethylene glycol ether groups and 10 to 100 propylene glycol ether groups, with 1 to 10 carbon atoms in the alkyl chain. The said compounds normally contain 1 to 5 ethylene glycol units per propylene glycol unit.

[0102] Examples of non-ionic surfactants which may be mentioned are nonylphenol polyethoxy ethanols, castor oil polyglycol ether, polypropylene-polyethylene oxide adducts, tributyl-phenoxy-polyethoxy ethanol, polyethylene glycol and octylphenoxy-polyethoxy ethanol.

[0103] Fatty acid esters of polyoxyethylene sorbitan, such as polyoxyethylene sorbitan trioleate, may also be considered.

[0104] The cationic surfactants in question are in particular quaternary ammonium salts, which contain as the N-substituents at least one alkyl radical with 8 to 22 C-atoms and as further substituents low, optionally halogenated alkyl, benzyl or low hydroxyalkyl radicals. The salts are preferably present as halides, methyl sulphates or ethyl sulphates, e.g. stearyl trimethylammonium chloride or benzyl-di-(2-chloroethyl)-ethylammonium bromide.

[0105] The surfactants which are customary in formulation techniques and which may also be used in the compositions according to the invention are described *inter alia* in "Mc Cutcheon's Detergents and Emulsifiers Annual" MC Publishing Corp., Ridgewood New Jersey, 1981, Stache, H., "Tensid-Taschenbuch", Carl Hanser Verlag, Munich/Vienna, 1981 and M. and J. Ash, "Encyclopedia of Surfactants", Vol I-III, Chemical Publishing Co., New York, 1980-81.

[0106] The herbicide formulations normally contain 0.1 to 99 % by weight, especially 0.1 to 95% by weight of active ingredient mixture comprising the compounds of formulae II to VI with the compounds of formula I, 1 to 99.9 % by weight of a solid or liquid formulation assistant and 0 to 25 % by weight, especially 0.1 to 25% by weight of a surfactant.

[0107] While concentrated compositions are usually preferred as a commercial product, the final user normally uses diluted formulations.

[0108] The compositions may also contain further additives such as stabilizers, e.g. optionally epoxidated vegetable oils (epoxidated coconut oil, rapeseed oil or soybean oil), defoamers, e.g. silicone oil, preservatives, viscosity regulators, binding agents, adhesives, as well as fertilizers or other active ingredients.

[0109] In order to employ antidotes of formula I or compositions containing them for the protection of cultivated plants from the damaging activity of herbicides of formulae II to VI, various methods and techniques may be considered, for example the following ones:

I) Seed dressing

[0110]

a) Dressing the seeds with an active ingredient of formula I formulated as a wettable powder, by shaking in a vessel until evenly distributed on the seed surface (dry treatment). Here, about 1 to 500 g of active ingredient of formula I (4 g to 2 kg wettable powder) are used per 100 kg of seed grain.

b) Dressing the seeds with an emulsion concentrate of the active ingredient of formula I according to method a) (wet treatment).

c) Dressing by immersing the seed grain in a liquid with 100-1000 ppm active ingredient of formula I for 1 to 72 hours and optionally subsequently drying the seeds (dressing by immersion).

[0111] Dressing the seed grain or treatment of the germinated seedling are of course the preferred methods of

application, since the treatment with active ingredient is aimed wholly at the target culture. It is customary to use 1 to 1000g antidote, preferably 5 to 250 g antidote, per 100 kg seed grain, whereby depending on the method, which also enables other active ingredients or micro-nutrients to be added, deviations above or below the concentration limits indicated may be allowed (repeat dressing).

ii) Application as a tank mixture

[0112] A liquid formulation of a mixture of antidote and herbicide (reciprocal ratio from 10:1 to 1:100) is used, whereby the amount of herbicide applied is 0.005 to 5.0 kg per hectare. Such tank mixtures are applied before or after sowing.

iii) Application in the furrow

[0113] The antidote is applied to the open furrow as an emulsion concentrate, wettable powder or granulate. After covering the furrow, the herbicide is applied in the usual manner in a pre-emergence process.

iv) Controlled release of active ingredient

[0114] The active ingredient of formula I in solution is absorbed onto mineral granulate carriers or polymerised granulated materials (urea/formaldehyde) and dried. If required, a coating may be applied (coated granules) which enables the active ingredient to be dispensed in a controlled release over a certain period.

[0115] The preferred formulations are made up in particular as follows:
(% = percent by weight)

Emulsifiable concentrates:	
active ingredient mixture	1 to 90%, preferably 5 to 20%
surface-active agent	1 to 30%, preferably 10 to 20%
liquid carrier	5 to 94%, preferably 70 to 85%

Dusts:	
active ingredient mixture:	0.1 to 10%, preferably 0.1 to 5%
solid carrier:	99.9 to 90%, preferably 99.9 to 99%

Suspension concentrates:	
active ingredient mixture	5 to 75%, preferably 10 to 50%
water	94 to 24%, preferably 88 to 30%
surface-active agent	1 to 40%, preferably 2 to 30%

Wettable powders:	
active ingredient mixture	0.5 to 90%, preferably 1 to 80%
surface-active agent	0.5 to 20%, preferably 1 to 15%
solid carrier material	5 to 95%, preferably 15 to 90%

Granulates:	
active ingredient mixture	0.1 to 30%, preferably 0.1 to 15%
solid carrier material	99.5 to 70%, preferably 97 to 85%

[0116] The following examples illustrate the invention further without restricting it.

Formulation examples for mixtures comprising herbicides of formulae II to VI and antidotes of formula I (% = percent by weight)

[0117]

F1. Emulsion concentrates	a)	b)	c)	d)
active ingredient mixture of formula I and II, III, IV, V or VI	5%	10%	25%	50%
Ca dodecylbenzene sulphonate	6%	8%	6%	8%
castor oil polyglycol ether (36 mols EO)	4%	--	4%	4%
octylphenol polyglycol ether (7-8 mols EO)	--	4%	--	2%
cyclohexanone	--	--	10%	20%
arom. hydrocarbon mixture C_9-C_{12}	85%	78%	55%	16%

[0118] Emulsions of each desired concentration may be produced from such concentrates by dilution with water.

F2. Solutions	a)	b)	c)	d)
active ingredient mixture of formula I and II, III, IV, V or VI	5%	10%	50%	90%
1-methoxy-3-(3-methoxy-propoxy)-propane	--	20%	20%	--
polyethylene glycol MW 400	20%	10%	--	--
N-methyl-2-pyrrolidone	--	--	30%	10%
arom. hydrocarbon mixture C_9-C_{12}	75%	60%		

[0119] The solutions are suitable for application in the form of the smallest droplets.

F3. Wettable powders	a)	b)	c)	d)
active ingredient mixture of formula I and II, III, IV, V or VI	5%	25%	50%	80%
Na lignin sulphonate	4%	--	3%	--
Na lauryl sulphate	2%	3%	--	4%
Na diisobutyl naphthalene sulphonate	--	6%	5%	6%
octylphenyl polyglycol ether (7-8 mols EO)	--	1%	2%	--
highly disperse silicic acid	1%	3%	5%	10%
kaolin	88%	62%	35%	--

[0120] The active ingredient is mixed well with the adjuvants and ground well in an appropriate mill. Wettable powders are obtained, which may be diluted with water to suspensions of any desired concentration.

F4. Coated granules	a)	b)	c)
active ingredient mixture of formula I and II, III, IV, V or VI	0.1%	5%	15%
highly disperse silicic acid	0.9%	2%	2%
inorg. carrier material (Ø 0.1 - 1 mm) such as $CaCO_3$ or SiO_2	99.0%	93%	83%

[0121] The active ingredient is dissolved in methylene chloride, sprayed onto the carrier and the solvent subsequently evaporated in a vacuum.

F5. Coated granules	a)	b)	c)
active ingredient mixture of formula I and II, III, IV, V or VI	0.1%	5%	15%
polyethylene glycol MW 200	1.0%	2%	3%

(continued)

F5. Coated granules	a)	b)	c)
highly disperse silicic acid	0.9%	1%	2%
inorg. carrier material (Ø 0.1 - 1 mm) such as $CaCO_3$ or SiO_2	98.0%	92%	80%

[0122] The finely ground active ingredient is evenly applied in a mixer onto the carrier material which has been moistened with polyethylene glycol. In this way, dust-free coated granules are obtained.

F6. Extrusion granules	a)	b)	c)	d)
active ingredient mixture of formula I and II, III, IV, V or VI	0.1%	3%	5%	15%
Na lignin sulphonate	1.5%	2%	3%	4%
carboxymethyl cellulose	1.4%	2%	2%	2%
kaolin	97.0%	93%	90%	79%

[0123] The active ingredient is mixed with the additives, ground and moistened with water. This mixture is extruded and subsequently dried in a current of air.

F7. Dusting agent	a)	b)	c)
active ingredient mixture of formula I and II, III, IV, V or VI	0.1%	1%	5%
talc	39.9%	49%	35%
kaolin	60.0%	50%	60%

[0124] By mixing the active ingredient with the carrier materials and grinding in an appropriate mill, a dusting agent is obtained which is ready for use.

F8. Suspension concentrates	a)	b)	c)	d)
active ingredient mixture of formula I and II, III, IV, V or VI	3%	10%	25%	50%
ethylene glycol	5%	5%	5%	5%
nonylphenol polyglycol ether (15 mols EO)	--	1%	2%	--
Na lignin sulphonate	3%	3%	4%	5%
carboxymethyl cellulose	1 %	1%	1%	1%
37% aqueous formaldehyde solution	0.2%	0.2%	0.2%	0.2%
silicone oil emulsion	0.8%	0.8%	0.8%	0.8%
water	87%	79%	62%	38%

[0125] The finely ground active ingredient is intimately mixed with the additives. In this way, a suspension concentrate is obtained, from which suspensions of any desired concentration may be prepared by dilution with water.

[0126] It is often more practical to formulate the active ingredients of formulae II to VI and the mixture components of formula I individually and then, shortly prior to placing in the applicator, to bring them together in water in the desired mixture ratio as a "tank mixture".

[0127] The ability of the antidotes of formula I to protect cultivated plants from the phythotoxic activity of herbicides of formulae II to VI is illustrated in the following examples.

Biological examples

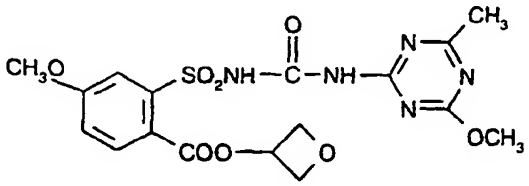
Example B1: Post-emergent application of mixtures of a herbicide of formulae II to VI with an antidote of formula I on cereals.

[0128] Wheat is raised in small plastic pots under glasshouse conditions up to the 2-5 leaf stage. At this stage, the herbicides of formulae II to VI are applied to the test plants both on their own and in a mixture with an antidote of formula I. Application takes place as an aqueous suspension of the test substances (formulation example F8) with 500 l water/ha. The test is evaluated 21 days after application using a nine-stage appraisal scale (1 = complete damage, 9 = no effect). Appraisal marks of 1 to 4 (especially 1 to 3) indicate strong phytotoxic activity. Appraisal marks of 5-9 (especially 7-9) indicate little to no phytotoxic damage of useful plants.

[0129] The results obtained show that with the antidote (3-oxo-isochroman-4-ylidenemethoxy)-acetic acid methyl ester (compound no. 01.002), the damage caused to wheat by the herbicide clodinafop can be considerably reduced.

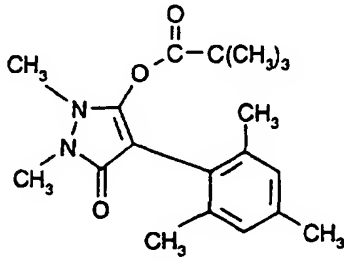
[0130] The same results are obtained if (3-oxo-isochroman-4-ylidenemethoxy)-acetic acid methyl ester (compound no. 01.002) and clodinafop are formulated according to examples F1 to F7.

[0131] Equally good results are obtained for the combinations (3-oxo-isochroman-4-ylidenemethoxy)-acetic acid methyl ester (compound no. 01.002) with primisulfuron, chlorimuron or with the compound of formula



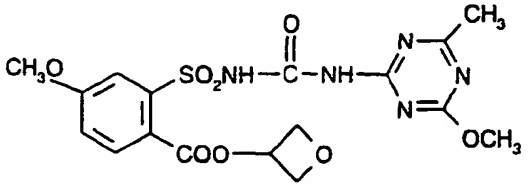
(IIIa)

or



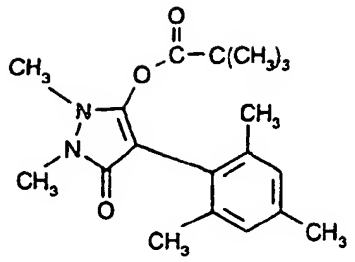
(Comp. No. 1.3),

as well as for the combinations (2-oxo-indan-1-ylidenemethoxy)-acetic acid methyl ester (compound no. 02.004) with clodinafop, primisulfuron, chlorimuron or with the compound of formula



(IIIa)

or



(Comp. No. 1.3)

[0132] The following Tables B1 to B5 illustrate the good antidote effect of the compounds of formula I in a mixture with the herbicides of formulae II, III and VI.

Table B1:

Post-emergent phytotoxic activity of the herbicides of formula II on the example clodinafop and the mixtures of clodinafop with antidotes of formula I on maize. The application rate for the herbicide clodinafop is 5 g/ha. The application rate for the antidotes of formula I is 250 g/ha.			
Herbicide [g/ha]		antidote [g/ha]	phytotoxic activity: maize
Clodinafop		---	1
Clodinafop	+	02.011	6
Clodinafop		---	2
Clodinafop	+	01.003	5
Clodinafop	+	01.005	7
Clodinafop	+	01.006	7
Clodinafop	+	02.004	9
Clodinafop	+	02.005	6
Clodinafop	+	03.003	9
Clodinafop	+	03.004	8
Clodinafop	+	03.006	6
Clodinafop		---	3
Clodinafop	+	01.002	6
Clodinafop	+	02.001	6
Clodinafop	+	02.002	6
Clodinafop		---	4
Clodinafop	+	01.007	9
Clodinafop	+	01.008	8
Clodinafop	+	+ 01.012	7
Clodinafop	+	01.013	7
Clodinafop	+	04.004	7
Clodinafop	+	04.005	7

Table B2:

Post-emergent phytotoxic activity of the herbicides of formula II on the example clodinafop and the mixtures of clodinafop with antidotes of formula I on rice. The application rate for the herbicide clodinafop is 60 g/ha. The application rate for the antidotes of formula I is 250 g/ha.		
Herbicide [g/ha]	antidote [g/ha]	phytotoxic activity: rice
Clodinafop	---	2

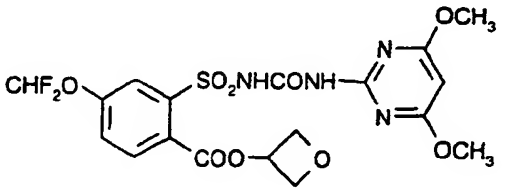
Table B2: (continued)

Post-emergent phytotoxic activity of the herbicides of formula II on the example clodinafop and the mixtures of clodinafop with antidotes of formula I on rice. The application rate for the herbicide clodinafop is 60 g/ha. The application rate for the antidotes of formula I is 250 g/ha.		
Herbicide [g/ha]	antidote [g/ha]	phytotoxic activity: rice
Clodinafop +	02.011	6
Clodinafop	---	3
Clodinafop +	01.006	6
Clodinafop	---	4
Clodinafop +	01.007	7
Clodinafop +	04.003	6
Clodinafop +	04.004	6
Clodinafop +	04.005	6

Table B3:

Post-emergent phytotoxic activity of the herbicides of formula III on the example of the compound of formula IIIa and the mixtures of compounds of formula IIIa with antidotes of formula I on rice. The application rate for the herbicide IIIa is 125 g/ha. The application rate for the antidotes of formula I is 250 g/ha.		
Herbicide [g/ha]	antidote [g/ha]	phytotoxic activity: rice
IIIa	---	3
IIIa +	01.001	4
IIIa +	01.003	5

Table B4: Post-emergent phytotoxic activity of the herbicides of formula III on the example of the compound of formula IIIe



(IIIe)

and the mixtures of compounds of formula IIIe with antidotes of formula I on maize. The application rate for the herbicide IIIe is 25 g/ha. The application rate for the antidotes of formula I is 250 g/ha.

Herbicide [g/ha]		antidote [g/ha]	phytotoxic activity: maize
IIIe		---	3
IIIe	+	02.004	5
IIIe	+	03.004	6
IIIe		---	4
IIIe	+	01.013	7
IIIe		---	5
IIIe	+	02.009	7
IIIe	+	02.011	7

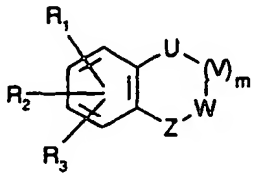
Table B5:

Post-emergent phytotoxic activity of the herbicides of formula VI on the example of the compound aRS, 1'S(-)N-(1'-methyl-2'-methoxyethyl)-N-chloracetyl-2-ethyl-6-methylaniline (VIa) and the mixtures of compound aRS,1'S(-)N-(1'-methyl-2'-methoxyethyl)-N-chloracetyl-2ethyl-6-methylaniline (VIa) with antidotes of formula I on maize. The application rate for the herbicide VIa is 5 g/ha. The application rate for the antidotes of formula I is 250 g/ha.

Herbicide [g/ha]		antidote [g/ha]	phytotoxic activity: maize
VIa		---	3
VIa	+	01.002	5
VIa	+	02.004	5

Claims

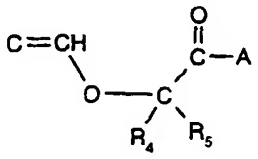
1. Compounds of formula I



(I),

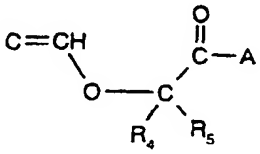
wherein
R_1 is hydrogen, C_1-C_4-alkyl, C_1-C_4-alkyl substituted by C_1-C_4-alkyl-X- or C_1-C_4-halogen-alkyl-X-, C_1-C_4-halogen-alkyl, nitro, cyano, -$COOR_8$, -NR_9R_{10}, -$SO_2NR_{11}R_{12}$ or -$CONR_{13}R_{14}$;
R_2 is hydrogen, halogen, C_1-C_4-alkyl, trifluoromethyl, C_1-C_4-alkoxy or C_1-C_4-halogen-alkoxy;
R_3 is hydrogen, halogen or C_1-C_4-alkyl;

U, V, W and Z, independently of one another, are oxygen, sulphur, $C(R_{15})R_{16}$, carbonyl, NR_{17} or a group



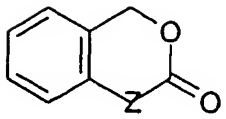
with the provisos that

a) at least one of the ring members U, V, W or Z is carbonyl, and one ring member which is adjacent to this or these ring members signifies the group



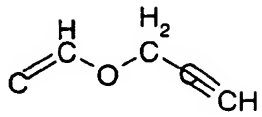
whereby this group only appears once; and

b) two adjacent ring members U and V, V and W and W and Z cannot simultaneously signify oxygen;
R_4 and R_5, independently of one another, signify hydrogen or C_1-C_8-alkyl; or
R_4 and R_5 together form a C_2-C_6-alkylene group;
A is R_7-Y- or $-NR_{18}R_{19}$;
X is oxygen or $-S(O)_p$;
Y is oxygen or sulphur;
R_7 is hydrogen, C_1-C_8-alkyl, C_1-C_8-halogen-alkyl, C_1-C_4-alkoxy-C_1-C_8-alkyll C_3-C_6-alkenyloxy-C_1-C_8-alkyl or phenyl-C_1-C_8-alkyl, whereby the phenyl ring may be substituted by halogen, C_1-C_4-alkyl, trifluoromethyl, methoxy or methyl-$S(O)_p$-; C_3-C_6-alkenyl, C_3-C_6-halogen-alkenyl, phenyl-C_3-C_6-alkenyl, C_3-C_6-alkinyl, phenyl-C_3-C_6-alkinyl, oxetanyl, furfuryl or tetrahydrofurfuryl;
R_8 is hydrogen or C_1-C_4-alkyl;
R_9 is hydrogen, C_1-C_4-alkyl or C_1-C_4-alkylcarbonyl;
R_{10} is hydrogen or C_1-C_4-alkyl; or
R_9 and R_{10} together form a C_4- or C_5-alkylene group;
R_{11}, R_{12}, R_{13} and R_{14}, independently of one another, are hydrogen or C_1-C_4-alkyl; or R_{11} together with R_{12} or R_{13} together with R_{14}, independently of one another, are C_4- or C_5-alkylene, whereby one carbon atom may be replaced by oxygen or sulphur, or one or two carbon atoms may be replaced by $-NR_{15}$-;
R_{15} and R_{16}, independently of one another, are hydrogen or C_1-C_8-alkyl; or
R_{15} and R_{16} together are C_2-C_6-alkylene;
R_{17} is hydrogen, C_1-C_8-alkyl, optionally substituted phenyl or benzyl optionally substituted on the phenyl ring;
R_{18} is hydrogen, C_1-C_8-alkyl, phenyl, phenyl-C_1-C_8-alkyl, whereby the phenyl rings may be substituted by fluorine, chlorine, bromine, nitro, cyano, $-OCH_3$, C_1-C_4-alkyl or CH_3SO_2-; C_1-C_4-alkoxy-C_1-C_8-alkyl, C_3-C_6-alkenyl, C_3-C_6-alkinyl or C_3-C_6-cycloalkyl;
R_{19} is hydrogen, C_1-C_8-alkyl, C_3-C_6-alkenyl or C_3-C_6-alkinyl; or
R_{18} and R_{19} together are C_4- or C_5-alkylene, whereby one carbon atom may be replaced by oxygen or sulphur, or one or two carbon atoms may be replaced by $-NR_{20}$-;
R_{20} is hydrogen or C_1-C_4-alkyl;
m is 0 or 1; and
p signifies 0, 1 or 2,
the compounds of formula I_{01a}

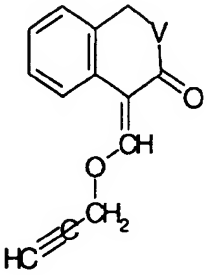


(I_{01a}),

wherein Z is a group C=CH-O-CH_2CH=CH_2,

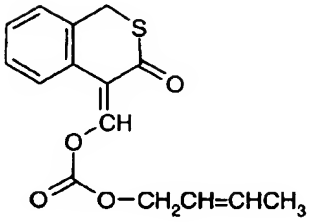


or C=CH-O-C(O)OCH_2CH=$CHCH_3$,
the compounds of formula I_{01b}

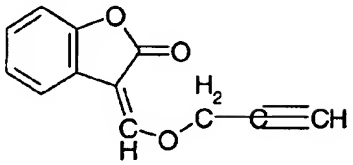


(I_{01b}),

wherein V is sulfur or NCH_3, and the 4 individual compounds no. 01.161

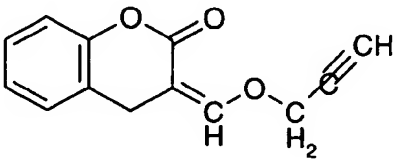


(01.161), 02.002



(02.002),

03.001



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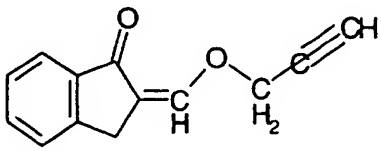


(04.003),

as well as agronomically compatible salts and stereoisomers of these compounds.

2. Compounds according to claim 1, wherein R_{17} is hydrogen or C_1-C_8-alkyl; and R_{18} is hydrogen, C_1-C_8-alkyl, phenyl, phenyl-C_1-C_8-alkyl, whereby the phenyl rings may be substituted by fluorine, chlorine, bromine, nitro, cyano, -OCH_3, C_1-C_4-alkyl or CH_3SO_2-; C_1-C_4-alkoxy-C_1-C_8-alkyl, C_3-C_6-alkenyl or C_3-C_6-alkinyl.

3. Compounds according to claim 1, wherein R_4 and R_5 are hydrogen.

4. Compounds according to claim 1, wherein A is R_7-Y-.

5. Compounds according to claim 4, wherein Y is oxygen.

6. Compounds according to claim 1, wherein U is $C(R_{15})R_{16}$.

7. Compounds according to claim 1, wherein R_{15} and R_{16} signify hydrogen.

8. Compounds according to claim 1, wherein m is 1, and V is oxygen or sulphur.

9. Compounds according to claim 1, wherein m is 0.

10. Compounds according to claim 1, wherein R_1 to R_5 are hydrogen, m is 1, V is oxygen, U is $C(R_{15})R_{16}$ and A is R_7-Y-.

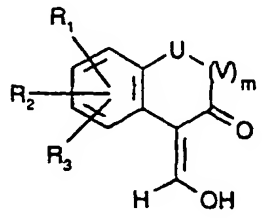
11. Compound according to claim 10, wherein R_{15} and R_{16} signify hydrogen; R_7 is methyl and Y is oxygen.

12. Compounds according to claim 1, wherein U is $C(R_{15})R_{16}$, m is 0, and R_1 to R_5 and A are defined as in claim 1.

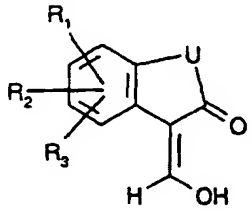
13. Compounds according to claim 12, wherein R_1 to R_5, R_{15} and R_{16} are hydrogen, and A is R_7-Y-.

14. Compound according to claim 13, wherein R_7 is methyl and Y is oxygen.

15. Process for the production of compounds of formula I according to claim 1, **characterised in that** a compound of formula VIIa or VIIb

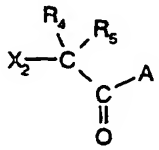


(VIIa) or



(VIIb),

wherein R_1 to R_3, U, V and m have the significances given in claim 1, is allowed to react with a compound of formula X



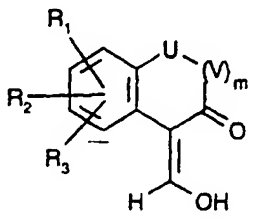
(X),

wherein R_4, R_5 and A have the significances given in claim 1, and X_2 signifies a leaving group,

a) in the presence of a base and an organic solvent at temperatures of 0° to 100°C, or

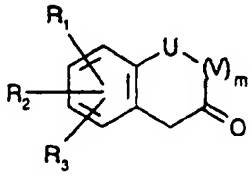
b) in the presence of an excess of cesium fluoride in an organic solvent at temperatures of 0° to 50°C.

16. Process for the production of compounds of formula VIIa



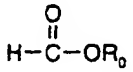
(VIIa),

wherein R_1 to R_3, U and V have the significances given in claim 1 and m is 1, **characterised in that** a compound of formula XIa



(XIa),

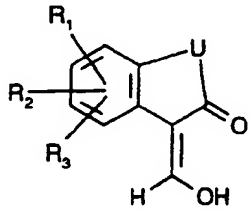
wherein R_1 to R_3, U, V and m have the significances indicated, is reacted with a compound of formula VIII



(VIII),

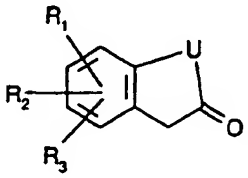
wherein R_0 is C_1-C_4-alkyl, in the presence of a base and optionally an organic solvent.

17. Process for the production of compounds of formula VIIb



(VIIb),

wherein R_1 to R_3 and U have the significances given in claim 1, **characterised in that** a compound of formula XIb

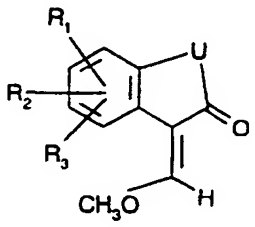


(XIb),

wherein R_1 to R_3 and U have the indicated significances, is reacted with a compound of formula IX

$$H\text{-}C(OCH_3)_3 \qquad (IX),$$

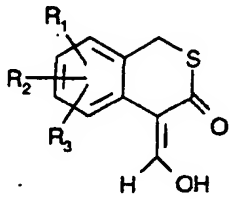
in the presence of an excess of acetic acid anhydride at an elevated temperature for 2 to 24 hours, to form the compound of formula VIIc



(VIIc)

and this compound undergoes enol ether cleavage with an aqueous base at 0° to 25°C, and is subsequently worked up under acidic conditions.

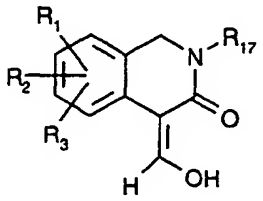
18. Compounds of formula $VIIa_1$



($VIIa_1$),

wherein R_1, R_2 and R_3 have the significances given in claim 1.

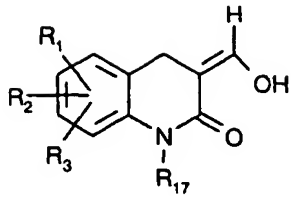
19. Compounds of formula $VIIa_2$



($VIIa_2$),

wherein R_1, R_2, R_3 and R_{17} have the significances given in claim 1.

20. Compounds of formula $VIIa_3$



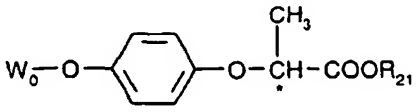
(VIIa$_3$),

wherein R_1, R_2, R_3 and R_{17} have the significances given in claim 1.

21. Usage of the compounds of formula I as herbicidal antidotes in herbicidal compositions.

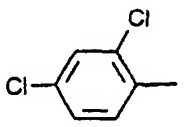
22. Composition having selective herbicide activity, **characterised in that**, in addition to the usual inert formulation assistants, it contains as active ingredient a herbicidal antidote of formula I according to claim 1 .

23. Composition having selective herbicide activity according to claim 22, **characterised in that** it contains a further active ingredient selected from the compounds of formulae II to VII

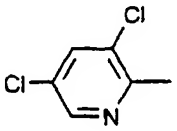


(II),

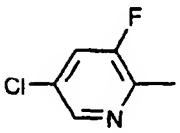
wherein
R_{21} signifies C_1-C_4-alkyl, propargyl or the group -CH_2-CH_2-O-N=$C(CH_3)_2$ and
W_o signifies the groups



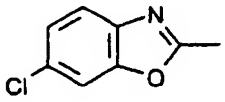
(W_1);



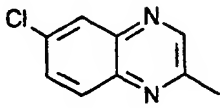
(W_2),



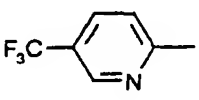
(W_3),



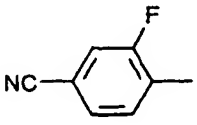
(W_4),



(W_5),

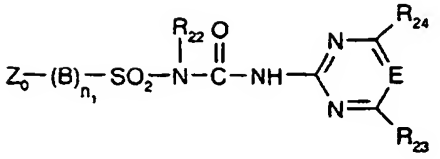


(W_6) or



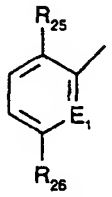
(W_7) ,

and in particular the R-enantiomers of these compounds; or of formula III

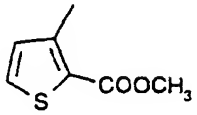


(III),

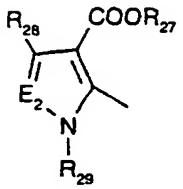
wherein Z_0 signifies a group



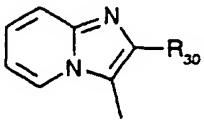
(Z_1),



(Z_2),

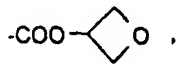


(Z_3),



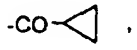
(Z_4) or CH_3-SO_2- (Z_5);

R_{22} signifies hydrogen or CH_3;
R_{23} signifies CH_3, -OCH_3, -$OCHF_2$, Cl, -$N(CH_3)_2$, -$NHCH_3$ or CF_3;
R_{24} signifies CH_3, -OCH_3, -$OCHF_2$, -OCH_2CF_3 or -OC_2H_5;
R_{25} signifies -OC_2H_5, -OCH_2CH_2Cl, -$COOCH_3$, -$COOC_2H_5$,



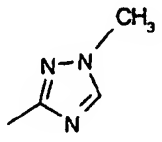
,

-O-CH_2CH_2-O-CH_3, Cl, -$CON(CH_3)_2$, -$SO_2C_2H_5$, CF_3, -$OCHF_2$,



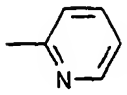
,

-$N(CH_3)SO_2CH_3$ or -$N(CH_3)COCH_3$;
R_{26} signifies hydrogen, CH_3, -OCH_3, CF_3, CHF_2 or -$OCHF_2$;
R_{27} signifies CH_3, C_2H_5 or the group



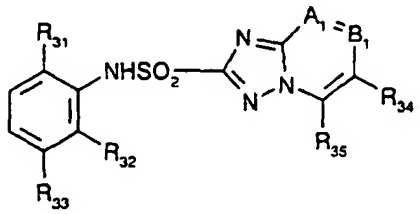
;

R_{28} signifies hydrogen or chlorine;
R_{29} signifies CH_3 or the group



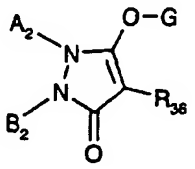
;

R_{30} signifies $-SO_2C_2H_5$ or chlorine;
E signifies nitrogen or methine;
E_1 signifies nitrogen, methine or $C-CH_3$;
E_2 signifies nitrogen or methine;
B signifies oxygen, -NH- or methylene; and
n_1 signifies 0 or 1,
as well as agronomically compatible salts of these compounds; or of formula IV



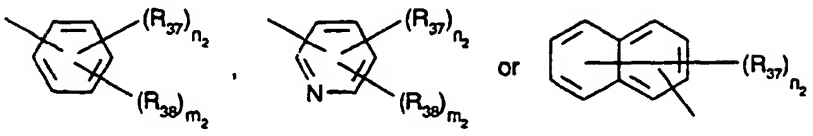
(IV),

wherein
R_{31} is fluorine or chlorine;
R_{32} is fluorine, chlorine or $-COOCH_3$;
R_{33} is hydrogen or methyl;
R_{34} is hydrogen or fluorine;
R_{35} is hydrogen or methoxy;
A_1 is nitrogen or $C-OC_2H_5$; and
B_1 is nitrogen, $C-CH_3$ or $C-OCH_3$; or of formula V



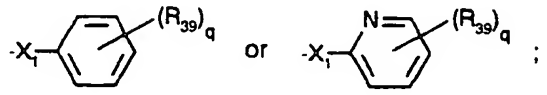
(V),

wherein
R_{36} signifies the group



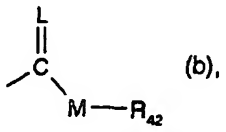
the substituents R_{37}, independently of one another, signify halogen, nitro, cyano, C_1-C_4-alkyl, C_1-C_4-halogen-alkyl, C_1-C_{10}-alkoxy, C_1-C_4-halogen-alkoxy, C_3-C_6-alkenyloxy, C_1-C_4-alkoxy-C_2-C_4-alkoxy, C_3-C_6-alkinyloxy, C_1-C_4-

alkylcarbonyl, C_1-C_4-alkoxycarbonyl, C_1-C_4-alkylthio, C_1-C_4-alkylsulphinyl, C_1-C_4-alkylsulphonyl, amino, C_1-C_4-alkylamino or di-C_1-C_4-alkylamino;
R_{38} signifies the group



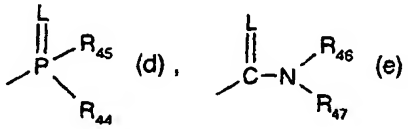
;

n_2 signifies 0, 1, 2, 3 or 4;
m_2 signifies 0 or 1, whereby the sum of m_2 and n_2 is 0, 1, 2, 3 or 4;
q signifies 0, 1, 2 or 3;
X_1 is oxygen, sulphur, $-CH_2-$ or $-N(R_{40})-$;
the substituents R_{39}, independently of one another, are C_1-C_4-alkyl, halogen, C_1-C_4-halogen-alkyl, C_1-C_4-alkoxy, C_1-C_4-halogen-alkoxy, nitro, cyano, C_1-C_4-alkoxycarbonyl, amino, C_1-C_4-alkylamino or di-C_1-C_4-alkylamino;
R_{40} signifies hydrogen, C_1-C_4-alkyl, formyl or C_1-C_4-alkylcarbonyl;
A_2 and B_2, independently of one another, signify hydrogen, alkyl, alkenyl, alkinyl, alkoxyalkyl, alkylthioalkyl or cycloalkyl, or optionally substituted aryl; or
A_2 and B_2 together form the bivalent radical of a saturated or unsaturated and optionally substituted mono-, bi-, tri- or polycyclic system;
G signifies hydrogen or the groups $-CO-R_{41}$ (a),

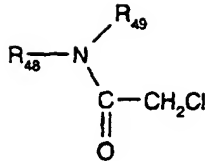


(b),

$-SO_2-R_{43}$ (c),

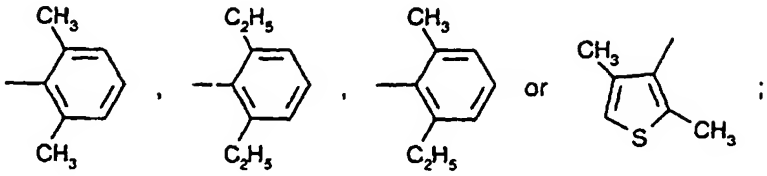


or M_1 (f)
L and M, independently of one another, are oxygen or sulphur;
R_{41} is halogen-alkyl, alkenyl, alkoxyalkyl, alkylthioalkyl, polyalkoxyalkyl or cycloalkyl, which may contain hetero atoms, optionally substituted phenyl, optionally substituted phenylalkyl, substituted heteroaryl, substituted phenoxyalkyl or substituted heteroaryloxyalkyl;
R_{42} is halogen-alkyl, alkenyl, alkoxyalkyl or polyalkoxyalkyl, or optionally substituted phenyl or benzyl;
R_{43}, R_{44} and R_{45}, independently of one another, are alkyl, halogen-alkyl, alkoxy, alkylamino, dialkylamino, alkylthio, alkenylthio, alkinylthio or cycloalkylthio, or optionally substituted phenyl, phenoxy or phenylthio;
R_{46} and R_{47}, independently of one another, are hydrogen, alkyl, halogen-alkyl, alkenyl, alkoxy or alkoxyalkyl, optionally substituted phenyl or benzyl; or
R_{46} and R_{47} together form an alkylene radical, which may optionally contain oxygen as a hetero atom; and
M_1 signifies a metal ion equivalent or an ammonium ion, as well as salts and diastereoisomers of the compounds of formula V; or of formula VI

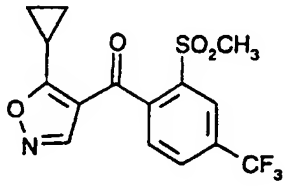


(VI),

wherein R_{48} signifies a group



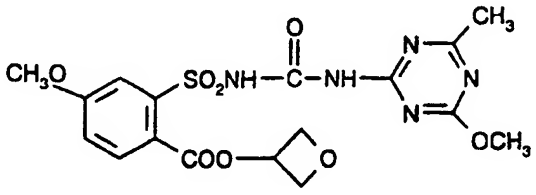
and
R_{49} signifies a group $-CH(CH_3)CH_2OCH_3$, $-CH_2OCH_3$ or $-CH_2OC_2H_5$; or of formula VII



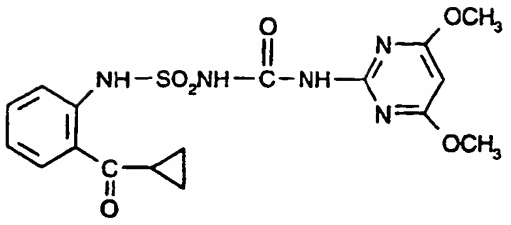
(VII).

24. Composition according to claim 23, **characterised in that** it contains clodinafop, quizalafop, propaquizafop, fenoxaprop, fluazifop and cyhalofop as the herbicides of formula II.

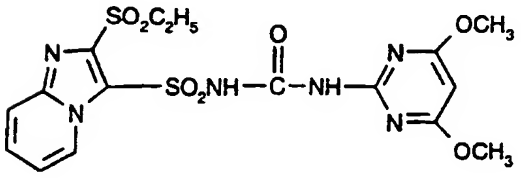
25. Composition according to claim 23, **characterised in that** it contains tribenuron, metsulfuron, primisulfuron, ethametsulfuron, sulfometuron, chlorimuron, oxasulfuron, triasulfuron, cinosulfuron, triflusulfuron, bensulfuron, ethoxysulfuron, sulfazuron, nicosulfuron, rimsulfuron, flupyrsulfuron, thifensulfuron, clopyrazosulfuron, pyrazosulfuron, sulfosulfuron, azimsulfuron und amidosulfuron as the herbicides of formula III, as well as the compounds of formulae IIIa to IIId



(IIIa),

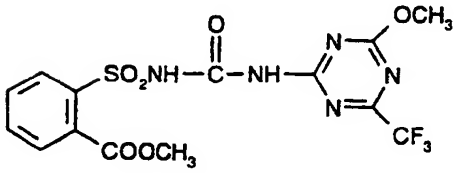


(IIIb),



(IIIc)

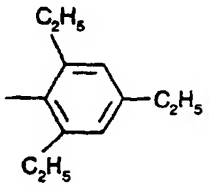
and



(IIId) .

26. Composition according to claim 23, **characterised in that** it contains flumetsulam, metosulam and cloransulam as compounds of formula IV.

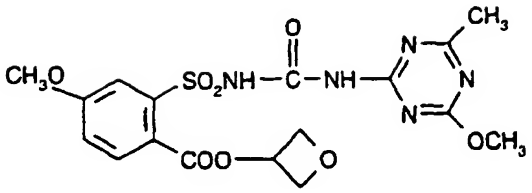
27. Composition according to claim 23, **characterised in that** in the compound of formula V, R_{36} is mesitylenyl or



A_2 and B_2 are methyl; or A_2 and B_2 together form a $-(CH_2)_4-$ group; and G signifies hydrogen or $-COC(CH_3)_3$.

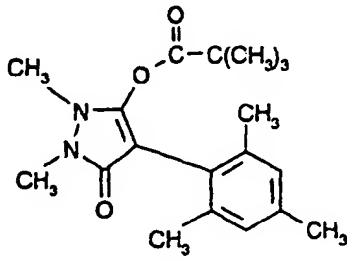
28. Composition according to claim 23, **characterised in that** it contains as the compound of formula VI metolachlor, alachlor, acetochlor, dimethenamide and in particular aRS,1'S(-)N-(1'-methyl-2'-methoxyethyl)-N-chloracetyl-2-ethyl-6-methylaniline.

29. Composition according to claim 23, **characterised in that** it contains as the compound of formula I (3-oxo-isochroman-4-ylidenemethoxy)-acetic acid methyl ester (compound no. 01.002) or (2-oxo-indan-1-ylidenemethoxy)-acetic acid methyl ester (compound no. 02.004), and as the active ingredient of formula II clodinafop, as the active ingredients of formula III primisulfuron, chlorimuron or the compound of formula



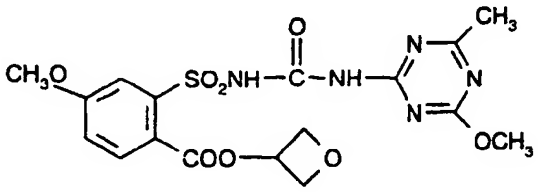
(IIIa)

and as the active ingredient of formula V the compound of formula



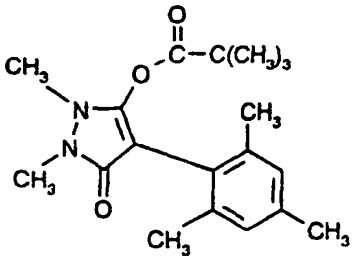
(Comp. no. 1.3).

30. Composition according to claim 23, **characterised in that** it contains as the compound of formula I (3-oxo-isochroman-4-ylidenemethoxy)-acetic acid methyl ester (compound no. 01.002), (2-oxo-indan-1-ylidenemethoxy)-acetic acid methyl ester (compound no. 02.004) or (3-oxo-isothiochroman-4-ylidenemethoxy)-acetic acid methyl ester (comp. no. 01.007) and as the active ingredient of formula II clodinafop, as the active ingredients of formula III primisulfuron, chlorimuron or the compound of formula



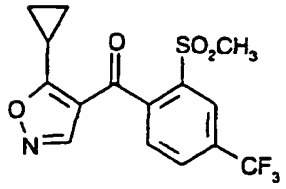
(IIIa)

and as the active ingredient of formula V the compound of formula



(Comp. no. 1.3)

and as the active ingredient the compound of formula VII



(VII) .

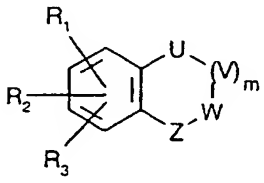
31. Process for the selective control of weeds and grasses in useful plant cultivations, **characterised in that** the useful plants, their seeds or cuttings or their cultivation area are treated simultaneously or separately with a herbicidally active amount of a herbicide of formula II, III, IV, V, VI or VII according to claim 23 and a herbicide-antagonistically active amount of an antidote of formula I according to claim 1.

32. Process according to claim 31, **characterised in that** useful plant cultivations or cultivation areas for the useful plant cultivations are treated with 0.001 to 2 kg/ha of a herbicide of formula II, III, IV, V, VI or VII and an amount of 0.001 to 0.5 kg/ha of an antidote of formula I.

33. Process according to claim 31, **characterised in that** the useful plant cultivations concerned are maize, cereals, soybeans or rice.

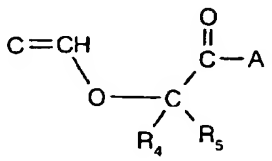
Patentansprüche

1. Verbindungen der Formel I



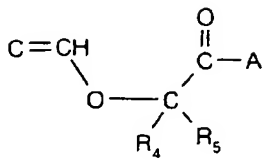
(I),

worin
R_1 Wasserstoff, C_1-C_4-Alkyl, C_1-C_4-Alkyl substituiert durch C_1-C_4-Alkyl-X- oder C_1-C_4-Halogenalkyl-X-, C_1-C_4-Halogenalkyl, Nitro; Cyano, $-COOR_8$, $-NR_9R_{10}$, $-SO_2NR_{11}R_{12}$ oder $-CONR_{13}R_{14}$;
R_2 Wasserstoff, Halogen, C_1-C_4-Alkyl, Trifluormethyl, C_1-C_4-Alkoxy oder C_1-C_4-Halogenalkoxy;
R_3 Wasserstoff, Halogen oder C_1-C_4-Alkyl ist;
U, V, W und Z unabhängig voneinander Sauerstoff, Schwefel, $C(R_{15})R_{16}$, Carbonyl, NR_{17} oder eine Gruppe



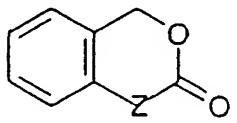
sind, mit den Massgaben, dass

a) mindestens eines der Ringglieder U, V, W oder Z Carbonyl ist, und ein zu diesem bzw. diesen Ringgliedern benachbartes Ringglied die Gruppe



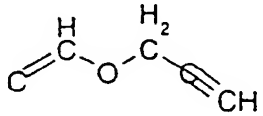
bedeutet, wobei diese Gruppe nur einmal vorkommt; und

b) zwei benachbarte Ringglieder U und V, V und W und W und Z nicht gleichzeitig Sauerstoff bedeuten können;
R_4 und R_5 unabhängig voneinander Wasserstoff oder C_1-C_8-Alkyl bedeuten; oder
R_4 und R_5 zusammen eine C_2-C_6-Alkylengruppe bilden;
A R_7-Y- oder -$NR_{18}R_{19}$;
X Sauerstoff oder -$S(O)_p$;
Y Sauerstoff oder Schwefel;
R_7 Wasserstoff, C_1-C_8-Alkyl, C_1-C_6-Halogenalkyl, C_1-C_4-Alkoxy-C_1-C_8-alkyl, C_3-C_6-Alkenyloxy-C_1-C_8-alkyl oder Phenyl-C_1-C_8-alkyl, wobei der Phenylring durch Halogen, C_1-C_4-Alkyl, Trifluormethyl, Methoxy oder Methyl-$S(O)_p$- substituiert sein kann, C_3-C_6-Alkenyl, C_3-C_6-Halogenalkenyl, Phenyl-C_3-C_6-alkenyl, C_3-C_6-Alkinyl, Phenyl-C_3-C_6-alkinyl, Oxetanyl, Furfuryl oder Tetrahydrofurfuryl;
R_8 Wasserstoff oder C_1-C_4-Alkyl;
R_9 Wasserstoff, C_1-C_4-Alkyl oder C_1-C_4-Alkylcarbonyl;
R_{10} Wasserstoff oder C_1-C_4-Alkyl ist; oder
R_9 und R_{10} zusammen eine C_4- oder C_5-Alkylengruppe bilden;
R_{11}, R_{12}, R_{13} und R_{14} unabhängig voneinander Wasserstoff oder C_1-C_4-Alkyl sind; oder R_{11} zusammen mit R_{12} oder R_{13} zusammen mit R_{14} unabhängig voneinander C_4- oder C_5-Alkylen sind, wobei ein Kohlenstoffatom durch Sauerstoff oder Schwefel, oder ein oder zwei Kohlenstoffatome durch -NR_{15}- ersetzt sein können;
R_{15} und R_{16} unabhängig voneinander Wasserstoff oder C_1-C_8-Alkyl sind; oder
R_{15} und R_{16} zusammen C_2-C_6-Alkylen sind;
R_{17} Wasserstoff, C_1-C_8-Alkyl, gegebenenfalls substituiertes Phenyl oder am Phenylring gegebenenfalls substituiertes Benzyl;
R_{18} Wasserstoff, C_1-C_8-Alkyl, Phenyl, Phenyl-C_1-C_8-alkyl, wobei die Phenylringe durch Fluor, Chlor, Brom, Nitro, Cyano, -OCH_3, C_1-C_4-Alkyl oder CH_3SO_2- substituiert sein können, C_1-C_4-Alkoxy-C_1-C_8-alkyl, C_3-C_6-Alkenyl, C_3-C_6-Alkinyl oder C_3-C_6-Cycloalkyl;
R_{19} Wasserstoff, C_1-C_8-Alkyl, C_3-C_6-Alkenyl oder C_3-C_6-Alkinyl ist; oder
R_{18} und R_{19} zusammen C_4- oder C_5-Alkylen sind, wobei ein Kohlenstoffatom durch Sauerstoff oder Schwefel, oder ein oder zwei Kohlenstoffatome durch -NR_{20}- ersetzt sein können;
R_{20} Wasserstoff oder C_1-C_4-Alkyl;
m 0 oder 1 ist; und
p 0, 1 oder 2 bedeutet, die Verbindungen der Formel I_{01a}



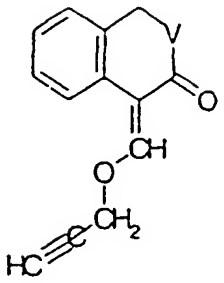
(I_{01a}),

worin Z eine Gruppe C=CH-O-CH_2CH=CH_2,



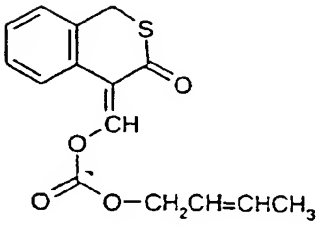
oder C=CH-O-C(O)OCH_2CH=$CHCH_3$ ist,

die Verbindungen der Formel I_{01b}

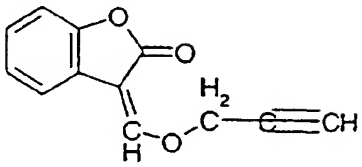


(I_{01b}),

worin V Schwefel oder NCH_3 ist, und die 4 einzelnen Verbindungen Nr. 01.161

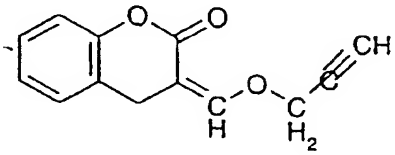


(01.161), 02.002

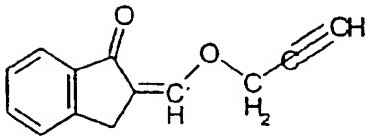


(02.002),

03.001



(03.001) und 04.003



(04.003),

sowie agronomisch verträgliche Salze und Stereoisomere dieser Verbindungen.

2. Verbindungen nach Anspruch 1, worin R_{17} Wasserstoff oder C_1-C_8-Alkyl; und R_{18} Wasserstoff, C_1-C_8-Alkyl, Phenyl, Phenyl-C_1-C_8-alkyl, wobei die Phenylringe durch Fluor, Chlor, Brom, Nitro, Cyano, -OCH_3, C_1-C_4-Alkyl oder CH_3SO_2- substituiert sein können, C_1-C_4-Alkoxy-C_1-C_8-alkyl, C_3-C_6-Alkenyl oder C_3-C_6-Alkinyl ist.

3. Verbindungen nach Anspruch 1, worin R_4 und R_5 Wasserstoff sind.

4. Verbindungen nach Anspruch 1, worin A R_7-Y- ist.

5. Verbindungen nach Anspruch 4, worin Y Sauerstoff ist.

6. Verbindungen nach Anspruch 1, worin U $C(R_{15})R_{16}$ ist.

7. Verbindungen nach Anspruch 1, worin R_{15} und R_{16} Wasserstoff bedeuten.

8. Verbindungen nach Anspruch 1, worin m 1; und V Sauerstoff oder Schwefel ist.

9. Verbindungen nach Anspruch 1, worin m 0 ist.

10. Verbindungen nach Anspruch 1, worin R_1 bis R_5 Wasserstoff sind; m 1; V Sauerstoff; U $C(R_{15})R_{16}$ und A R_7-Y- ist.

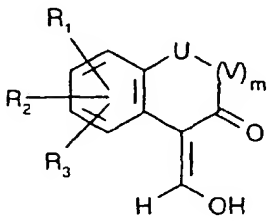
11. Verbindung nach Anspruch 10, worin R_{15} und R_{16} Wasserstoff bedeuten; R_7 Methyl; und Y Sauerstoff ist.

12. Verbindungen nach Anspruch 1, worin U $C(R_{15})R_{16}$; m 0 ist; und R_1 bis R_5 und A wie in Anspruch 1 definiert sind.

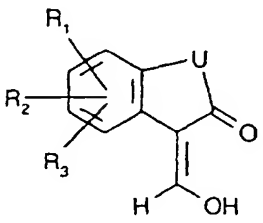
13. Verbindungen nach Anspruch 12, worin R_1 bis R_5, R_{15} und R_{16} Wasserstoff sind; und A R_7-Y- ist.

14. Verbindung nach Anspruch 13, worin R_7 Methyl; und Y Sauerstoff ist.

15. Verfahren zur Herstellung von Verbindungen der Formel I nach Anspruch 1, **dadurch gekennzeichnet, dass** man eine Verbindung der Formel VIIa oder VIIb

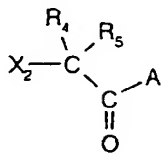


(VIIa) oder



(VIIb),

worin R_1 bis R_3, U, V und m die in Anspruch 1 angegebene Bedeutung haben, mit einer Verbindung der Formel X



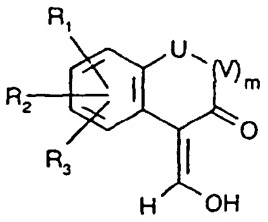
(X),

worin R_4, R_5 und A die in Anspruch 1 angegebene Bedeutung haben und X_2 eine Abgangsgruppe bedeutet,

a) in Gegenwart einer Base und eines organischen Lösungsmittels bei Temperaturen von 0° bis 100°C reagieren lässt, oder

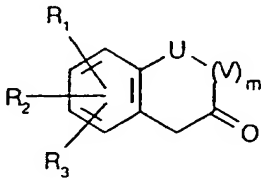
b) in Gegenwart eines Ueberschusses von Cäsiumfluorid in einem organischen Lösungsmittel bei Temperaturen von 0° bis 50°C reagieren lässt.

16. Verfahren zur Herstellung von Verbindungen der Formel VIIa



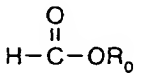
(VIIa),

worin R_1 bis R_3, U und V die in Anspruch 1 angegebene Bedeutung haben, und m 1 ist, **dadurch gekennzeichnet, dass** man eine Verbindung der Formel XIa



(XIa),

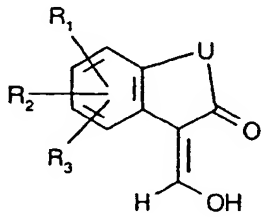
worin R_1 bis R_3, U, V und m die angegebene Bedeutung haben, mit einer Verbindung der Formel VIII



(VIII),

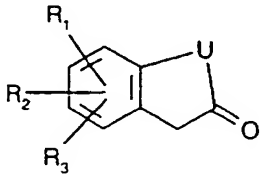
worin R_0 C_1-C_4-Alkyl ist, in Gegenwart einer Base und gegebenenfalls eines organischen Lösungsmittels umsetzt.

17. Verfahren zur Herstellung von Verbindungen der Formel VIIb



(VIIb),

worin R_1 bis R_3 und U die in Anspruch 1 angegebene Bedeutung haben, **dadurch gekennzeichnet, dass** man eine Verbindung der Formel XIb

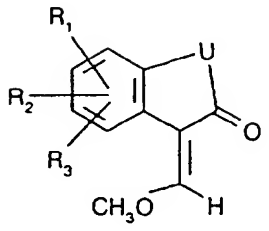


(XIb),

worin R_1 bis R_3 und U die angegebene Bedeutung haben, mit einer Verbindung der Formel IX

$$H\text{-}C(OCH_3)_3 \qquad (IX),$$

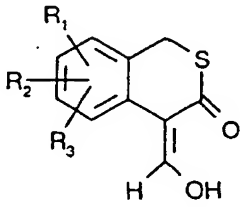
in Gegenwart eines Ueberschusses an Essigsäureanhydrid bei erhöhter Temperatur während 2 bis 24 Stunden zur Verbindung der Formel VIIc



(VIIc)

umsetzt, und diese mit wässriger Base bei 0° bis 25°C einer Enoletherspaltung unterwirft und anschliessend unter sauren Bedingungen aufarbeitet.

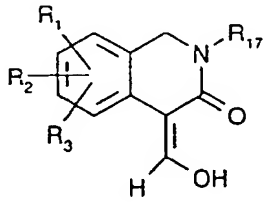
18. Verbindungen der Formel $VIIa_1$



($VIIa_1$),

worin R_1, R_2 und R_3 die in Anspruch 1 angegebene Bedeutung haben.

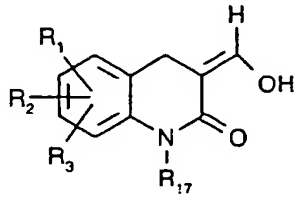
19. Verbindungen der Formel $VIIa_2$



($VIIa_2$),

worin R_1, R_2, R_3 und R_{17} die in Anspruch 1 angegebene Bedeutung haben.

20. Verbindungen der Formel $VIIa_3$



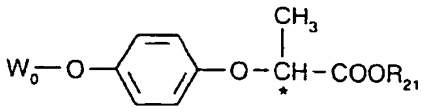
($VIIa_3$),

worin R_1, R_2, R_3 und R_{17} die in Anspruch 1 angegebene Bedeutung haben.

21. Verwendung der Verbindungen der Formel I als herbizide Safener in herbiziden Mitteln.

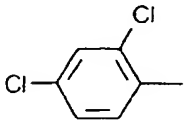
22. Selektiv-herbizides Mittel, **dadurch gekennzeichnet, daß** es neben üblichen inerten Formulierungshilfsmitteln als Wirkstoff einen herbiziden Safener der Formel 1 gemäß Anspruch 1 enthält.

23. Selektiv-herbizides Mittel nach Anspruch 22, **dadurch gekennzeichnet, daß** es einen weiteren Wirkstoff, ausgewählt aus den Verbindungen der Formeln II bis VII

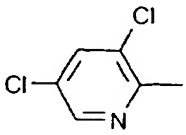


(II),

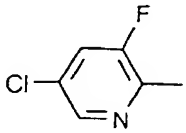
worin R_{21} C_1-C_4-Alkyl, Propargyl oder die Gruppe $-CH_2-CH_2-O-N=C(CH_3)_2$; und W_0 die Gruppen



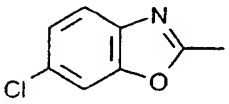
(W_1);



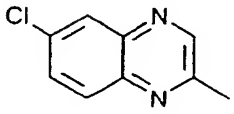
(W_2),



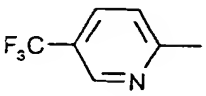
(W_3),



(W_4),

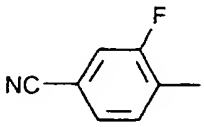


(W_5),

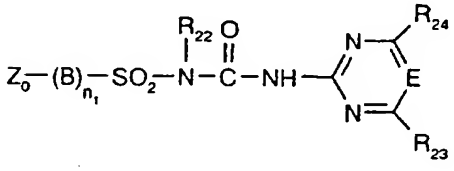


(W_6)

oder

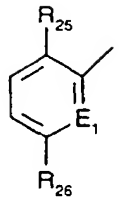
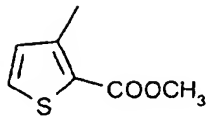
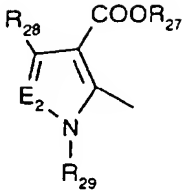


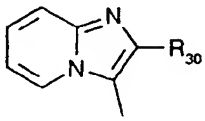
(W_7) bedeutet, und insbesondere die R-Enantiomeren dieser Verbindungen; oder der Formel III



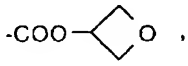
(III),

worin Z_o eine Gruppe

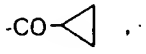

(Z1),

(Z2),

(Z3),


(Z4)

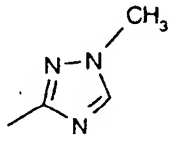
oder CH_3-SO_2- (Z_5);
R_{22} Wasserstoff oder CH_3;
R_{23} CH_3, -OCH_3, -$OCHF_2$, Cl, -$N(CH_3)_2$, -$NHCH_3$ oder CF_3;
R_{24} CH_3, -OCH_3, -$OCHF_2$, -OCH_2CF_3 oder -OC_2H_5;
R_{25} -OC_2H_5, -OCH_2CH_2Cl, -$COOCH_3$, -$COOC_2H_5$,


,

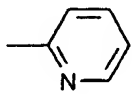
-O-CH_2CH_2-O-CH_3, Cl, -$CON(CH_3)_2$, -$SO_2C_2H_5$, CF_3, -$OCHF_2$,


,

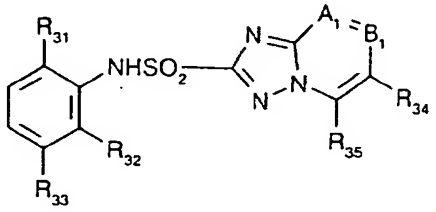
-$N(CH_3)SO_2CH_3$ oder -$N(CH_3)COCH_3$;
R_{26} Wasserstoff, CH_3, -OCH_3, CF_3, CHF_2 oder -$OCHF_2$;
R_{27} CH_3, C_2H_5 oder die Gruppe


;

R_{28} Wasserstoff oder Chlor;
R_{29} CH_3 oder die Gruppe

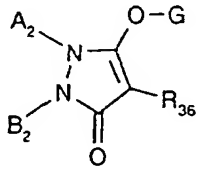

;

R_{30} $-SO_2C_2H_5$ oder Chlor;
E Stickstoff oder Methin;
E_1 Stickstoff, Methin oder $C-CH_3$;
E_2 Stickstoff oder Methin;
B Sauerstoff, -NH- oder Methylen; und
n_1 0 oder 1 bedeutet, sowie agronomisch verträgliche Salze dieser Verbindungen; oder der Formel IV



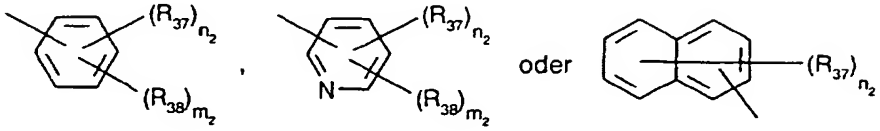
(IV),

worin
R_{31} Fluor oder Chlor;
R_{32} Fluor, Chlor oder $-COOCH_3$;
R_{33} Wasserstoff oder Methyl;
R_{34} Wasserstoff oder Fluor;
R_{35} Wasserstoff oder Methoxy;
A_1 Stickstoff oder $C-OC_2H_5$; und
B_1 Stickstoff, $C-CH_3$ oder $C-OCH_3$ ist; oder der Formel V

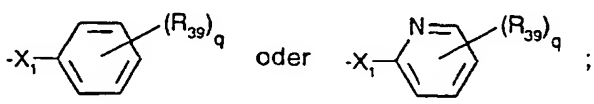


(V),

worin R_{36} die Gruppe

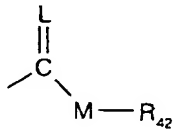


bedeutet; die Substituenten R_{37} unabhängig voneinander Halogen, Nitro, Cyano, C_1-C_4-Alkyl, C_1-C_4-Halogenalkyl, C_1-C_{10}-Alkoxy, C_1-C_4-Halogenalkoxy, C_3-C_6-Alkenyloxy, C_1-C_4-Alkoxy-C_2-C_4-alkoxy, C_3-C_6-Alkinyloxy, C_1-C_4-Alkylcarbonyl, C_1-C_4-Alkoxycarbonyl, C_1-C_4-Alkylthio, C_1-C_4-Alkylsulfinyl, C_1-C_4-Alkylsulfonyl, Amino, C_1-C_4-Alkylamino oder Di-C_1-C_4-alkylamino sind;
R_{38} die Gruppe

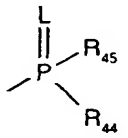


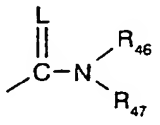
;

n_2 0, 1, 2, 3 oder 4;
m_2 0 oder 1, wobei die Summe von m_2 und n_2 0, 1, 2, 3 oder 4 ist;
q 0, 1, 2 oder 3;
X_1 Sauerstoff, Schwefel, $-CH_2-$ oder $-N(R_{40})-$ ist; die Substituenten R_{39} unabhängig voneinander C_1-C_4-Alkyl, Halogen, C_1-C_4-Halogenalkyl, C_1-C_4-Alkoxy, C_1-C_4-Halogenalkoxy, Nitro, Cyano, C_1-C_4-Alkoxycarbonyl, Amino, C_1-C_4-Alkylamino oder Di-C_1-C_4-alkylamino sind;
R_{40} Wasserstoff, C_1-C_4-Alkyl, Formyl oder C_1-C_4-Alkylcarbonyl bedeutet;
A_2 und B_2 unabhängig voneinander Wasserstoff, Alkyl, Alkenyl, Alkinyl, Alkoxyalkyl, Alkylthioalkyl oder Cycloalkyl, oder gegebenenfalls substituiertes Aryl; oder
A_2 und B_2 zusammen den bivalenten Rest eines gesättigten oder ungesättigten und gegebenenfalls substituierten mono-, bi-, tri- oder polycyclischen Systems bilden;
G Wasserstoff oder die Gruppen $-CO-R_{41}$ (a),

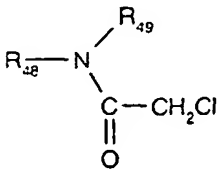

(b),

$-SO_2-R_{43}$ (c),

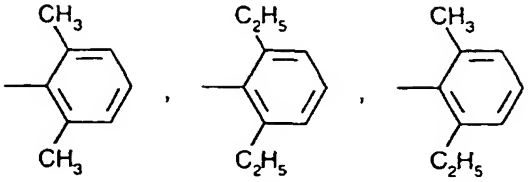

(d),


(e)

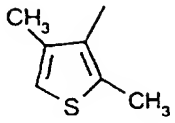
oder M_1 (f) bedeutet;
L und M unabhängig voneinander Sauerstoff oder Schwefel sind;
R_{41} Halogenalkyl, Alkenyl, Alkoxyalkyl, Alkylthioalkyl, Polyalkoxyalkyl oder Cycloalkyl, das Heteroatome enthalten kann, gegebenenfalls substituiertes Phenyl, gegebenenfalls substituiertes Phenylalkyl, substituiertes Heteroaryl, substituiertes Phenoxyalkyl oder substituiertes Heteroaryloxyalkyl;
R_{42} Halogenalkyl, Alkenyl, Alkoxyalkyl oder Polyalkoxyalkyl, oder gegebenenfalls substituiertes Phenyl oder Benzyl ist;
R_{43}, R_{44} und R_{45} unabhängig voneinander Alkyl, Halogenalkyl, Alkoxy, Alkylamino, Dialkylamino, Alkylthio, Alkenylthio, Alkinylthio oder Cycloalkylthio, oder gegebenenfalls substituiertes Phenyl, Phenoxy oder Phenylthio;
R_{46} und R_{47} unabhängig voneinander Wasserstoff, Alkyl, Halogenalkyl, Alkenyl, Alkoxy oder Alkoxyalkyl, gegebenenfalls substituiertes Phenyl oder Benzyl sind; oder
R_{46} und R_{47} zusammen einen Alkylenrest bilden, der gegebenenfalls als Heteroatom Sauerstoff enthalten kann; und
M_1 ein Metallionenäquivalent oder ein Ammoniumion bedeutet, sowie Salze und Diastereomere der Verbindungen der Formel V, oder der Formel VI


(VI),

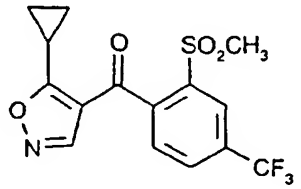
worin R_{48} eine Gruppe



oder



und R_{49} eine Gruppe $-CH(CH_3)CH_2OCH_3$, $-CH_2OCH_3$ oder $-CH_2OC_2H_5$ bedeutet, oder der Formel VII

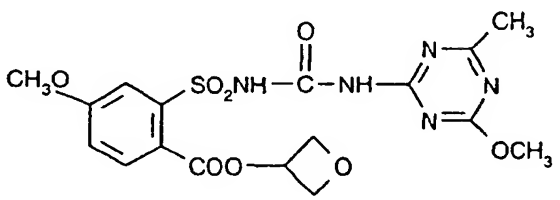


(VII),

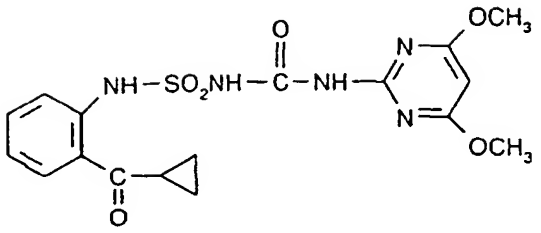
, enthält.

24. Mittel nach Anspruch 23, **dadurch gekennzeichnet, dass** es als die Herbizide der Formel II Clodinafop, Quizalafop, Propaquizafop, Fenoxaprop, Fluazifop und Cyhalofop enthält.

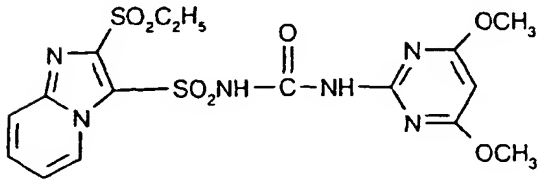
25. Mittel nach Anspruch 23, **dadurch gekennzeichnet, dass** es als die Herbizide der Formel III Tribenuron, Metsulfuron, Primisulfuron, Ethametsulfuron, Sulfometuron, Chlorimuron, Oxasulfuron, Triasulfuron, Cinosulfuron, Triflusulfuron, Bensulfuron, Ethoxysulfuron, Sulfazuron, Nicosulfuron, Rimsulfuron, Flupyrsulfuron, Thifensulfuron, Clopyrazosulfuron, Pyrazosulfuron, Sulfosulfuron, Azimsulfuron und Amidosulfuron, sowie die Verbindungen der Formeln IIIa bis IIId



(IIIa),

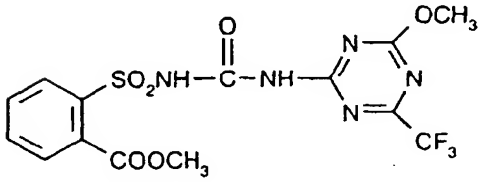


(IIIb),



(IIIc)

und

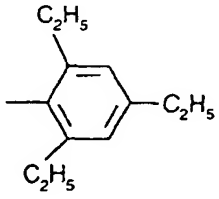


(IIId)

enthält.

26. Mittel nach Anspruch 23, **dadurch gekennzeichnet, dass** es als Verbindungen der Formel IV Flumetsulam, Metosulam und Cloransulam enthält.

27. Mittel nach Anspruch 23, **dadurch gekennzeichnet, dass** in der Verbindung der Formel V
R_{36} Mesitylenyl oder

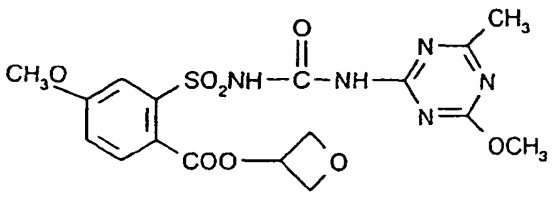


ist; A_2 und B_2 Methyl sind; oder A_2 und B_2 zusammen eine $-(CH_2)_4-$ Gruppe bilden; und G Wasserstoff oder -COC $(CH_3)_3$ bedeutet.

28. Mittel nach Anspruch 23, **dadurch gekennzeichnet, dass** es als Verbindung der Formel VI Metolachlor, Alachlor, Acetochlor, Dimethenamid und insbesondere aRS,1'S(-)N-(1'-Methyl-2'-methoxyethyl)-N-chloracetyl-2-ethyl-6-methylanilin enthält.

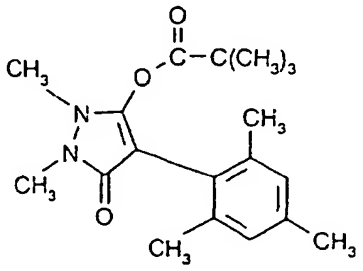
29. Mittel nach Anspruch 23, **dadurch gekennzeichnet, dass** es als Verbindung der Formel I (3-Oxo-isochroman-

4-ylidenmethoxy)-essigsäuremethylester (Verb. Nr. 01.002) oder (2-Oxo-indan-1ylidenmethoxy)-essigsäuremethylester (Verb. Nr. 02.004), und als Wirkstoff der Formel II Clodinafop, als Wirkstoffe der Formel III Primisulfuron, Chlorimuron oder die Verbindung der Formel



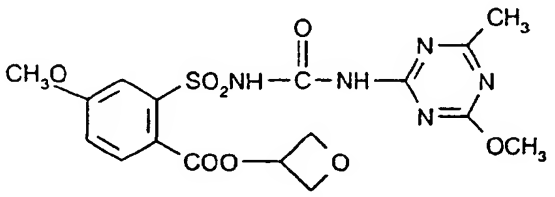
(IIIa),

und als Wirkstoff der Formel V die Verbindung der Formel



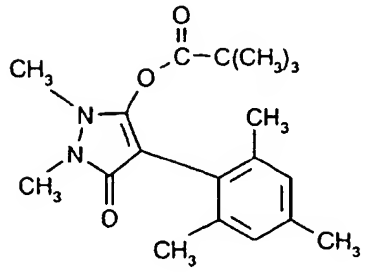
(Verb. Nr. 1.3) enthält.

30. Mittel nach Anspruch 23, **dadurch gekennzeichnet, dass** es als Verbindung der Formel I (3-Oxo-isochroman-4-ylidenmethoxy)-essigsäuremethylester (Verb. Nr. 01.002), (2-Oxo-indan-1ylidenmethoxy)-essigsäuremethylester (Verb. Nr. 02.004) oder (3-Oxo-isothiochroman-4-ylidenmethoxy)-essigsäuremethylester (Verb. Nr. 01.007), und als Wirkstoff der Formel II Clodinafop, als Wirkstoffe der Formel III Primisulfuron, Chlorimuron oder die Verbindung der Formel

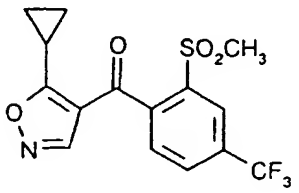


(IIIa),

als Wirkstoff der Formel V die Verbindung der Formel



(Verb. Nr. 1.3) und als Wirkstoff die Verbindung der Formel VII



(VII)

enthält.

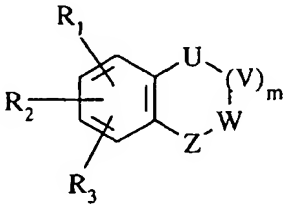
31. Verfahren zum selektiven Bekämpfen von Unkräutern und Gräsern in Nutzpflanzenkulturen, **dadurch gekennzeichnet, daß** man die Nutzpflanzen, deren Samen oder Stecklinge oder deren Anbaufläche gleichzeitig oder getrennt mit einer herbizid wirksamen Menge eines Herbizids der Formel II, III, IV, V, VI oder VII gemäß Anspruch 23 und einer herbizid-antagonistisch wirksamen Menge eines Safeners der Formel I gemäß Anspruch 1 behandelt.

32. Verfahren gemäß Anspruch 31, **dadurch gekennzeichnet, daß** man Nutzpflanzenkulturen oder Anbauflächen für die Nutzpflanzenkulturen mit 0,001 bis 2 kg/ha eines Herbizids der Formel II, III, IV, V, VI oder VII und einer Menge von 0,001 bis 0,5 kg/ha eines Safeners der Formel I behandelt.

33. Verfahren gemäß Anspruch 31, **dadurch gekennzeichnet, daß** es sich bei den Nutzpflanzenkulturen um Mais, Getreide, Soja oder Reis handelt.

Revendications

1. Composés de formule I



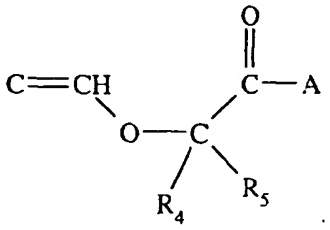
(I),

où

R_1 est hydrogène, alkyle en C_1-C_4, alkyle en C_1-C_4 substitué par (alkyl en C_1-C_4)-X- ou halogéno(alkyl en C_1-C_4)-X-, halogénoalkyle en C_1-C_4, nitro, cyano, $-COOR_8$, $-NR_9R_{10}$, $-SO_2NR_{11}R_{12}$ ou $-CONR_{13}R_{14}$;

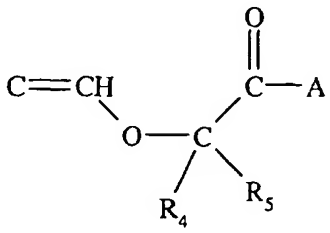
R_2 est hydrogène, halogène, alkyle en C_1-C_4, trifluorométhyle, alcoxy en C_1-C_4 ou halogénoalcoxy en C_1-C_4 ;

R_3 est hydrogène, halogène ou alkyle en C_1-C_4;
U, V, W et Z, indépendamment les uns des autres, sont oxygène, soufre, $C(R_{15})R_{16}$, carbonyle, NR_{17} ou un groupe



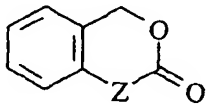
sous réserves que

a) au moins un des éléments de cycle U, V, W ou Z soit un carbonyle et un élément de cycle qui est adjacent à ce ou ces éléments de cycle représente le groupe



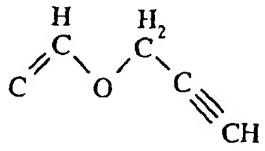
ce groupe n'apparaissant qu'une fois ; et
b) deux éléments de cycle adjacents U et V, V et W et W et Z ne puissent pas simultanément désigner un oxygène ;
R_4 et R_5, indépendamment l'un de l'autre. signifient hydrogène ou alkyle en C_1-C_8 ou
R_4 et R_5 forment ensemble un groupe alkylène en C_2-C_6;
A est R_7-Y-ou-$NR_{18}R_{19}$;
X est oxygène ou -$S(O)_p$;
Y est oxygène ou soufre ;
R_7 est hydrogène, alkyle en C_1-C_8, halogénoalkyle en C_1-C_8, (alcoxy en C_1-C_4)alkyle en C_1-C_8, (alcényl en C_3-C_6)oxyalkyle en C_1-C_8 ou phényl-(alkyle en C_1-C_8), où le cycle phényle peut être substitué par halogène, alkyle en C_1-C_4, trifluorométhyle, méthoxy ou inéthyl-$S(O)_p$-; alcényle en C_3-C_6, halogénoalcényle en C_3-C_6, phényl(alcényle en C_3-C_6), alcynyle en C_3-C_6, phényl(alcynyle en C_3-C_6), oxétanyle, furfuryle ou tétrahydro-furfuryle
R_8 est hydrogène ou alkyle en C_1-C_4 ;
R_9 est hydrogène, alkyle en C_1-C_4 ou (alkyl en C_1-C_4)carbonyle ;
R_{10} est hydrogène ou alkyle en C_1-C_4 ; ou
R_9 et R_{10} forment ensemble un groupe alkylène en C_4 ou C_5 ;
R_{11}, R_{12}, R_{13} et R_{14}, indépendamment les uns des autres, sont hydrogène ou alkyle en C_1-C_4 ;
ou R_{11} avec R_{12} ou R_{13} avec R_{14}, indépendamment l'un de l'autre, sont un groupe alkylène en C_4 ou C_5, un atome de carbone pouvant être remplacé par un oxygène ou un soufre, ou bien un ou deux atomes de carbone pouvant être remplacés par -NR_{15}- ;
R_{15} et R_{16}, indépendamment l'un de l'autre, sont hydrogène ou alkyle en C_1-C_8 ou
R_{15} et R_{16} forment ensemble un groupe alkylène en C_2-C_6;
R_{17} est hydrogène, alkyle en C_1-C_8, phényle éventuellement substitué ou benzyle éventuellement substitué sur le cycle phényle ;
R_{18} est hydrogène, alkyle en C_1-C_8, phényle. phényl(alkyle en C_1-C_8), où les cycles phényle peuvent être substitués par fluor, chlore, brome, nitro, cyano, -OCH_3, alkyle en C_1-C_4 ou CH_3SO_2-; (alcoxy en C_1-C_4)alkyle en C_1-C_8. alcényle en C_3-C_6, alcynyle en C_3-C_6 ou cycloalkyle en C_3-C_6;
R_{19} est hydrogène, alkyle en C_1-C_8, alcényle en C_3-C_6 ou alcynyle en C_3-C_6; ou

R_{18} et R_{19} forment ensemble un alkylène en C_4 ou C_5, un atome de carbone pouvant être remplacé par un oxygène ou un soufre, ou bien un ou deux atomes de carbone pouvant être remplacés par $-NR_{20}-$;
R_{20} est hydrogène ou alkyle en C_1-C_4 ;
m est 0 ou 1 ; et
p signifie 0, 1 ou 2, les composés de formule I_{01a}

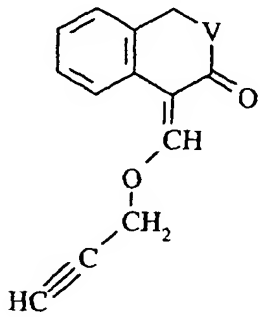


(I_{01a}),

où Z est un groupe $C=CH-O-CH_2CH=CH_2$,

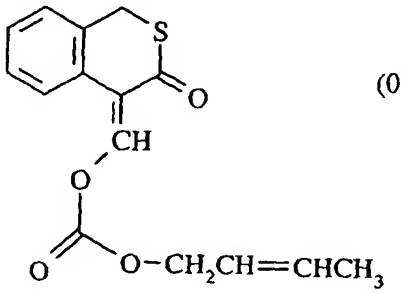


ou $C=CH-O-C(O)OCH_2CH=CHCH_3$, les composés de formule I_{01b}



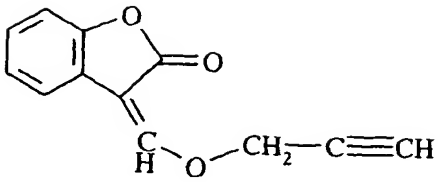
(I_{01b}),

où V est soufre ou NCH_3, et les 4 comnosés individuels n° 01 161



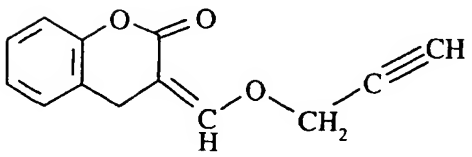
(01.161),

n° 02.002



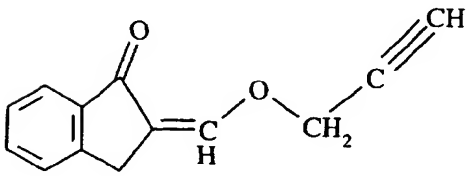
(02.002),

n° 03.001



(03.001),

et n° 04.003



(04.003),

ainsi que leurs sels compatibles en agronomie et les stéréoisomères de ces composés.

2. Composés selon la revendication 1, dans lesquels R_{17} est hydrogène ou alkyle en C_1-C_8 et R_{18} est hydrogène, alkyle en C_1-C_8, phényle, phényl(alkyle en C_1-C_8), où les cycles phényle peuvent être substitués par fluor, chlore, brome, nitro, cyano, -OCH_3, alkyle en C_1-C_4 ou CH_3SO_2-; (alcoxy en C_1-C_4)alkyle en C_1-C_8, alcényle en C_3-C_6 ou alcynyle en C_3-C_6.

3. Composés selon la revendication 1, dans lesquels R_4 et R_5 sont des atomes d'hydrogène.

4. Composés selon la revendication 1, dans lesquels A est R_7-Y-.

5. Composés selon la revendication 4, dans lesquels Y est oxygène.

6. Composés selon la revendication 1, dans lesquels U est $C(R_{15})R_{16}$.

7. Composés selon la revendication 1, dans lesquels R_{15} et R_{16} désignent des atomes d'hydrogène.

8. Composés selon la revendication 1, dans lesquels m est égal à 1 et V est oxygène ou soufre.

9. Composés selon la revendication 1, dans lesquels m est égal à 0.

10. Composés selon la revendication 1, dans lesquels R_1 à R_5 sont des atomes d'hydrogène, m est égal à 1, V est oxygène, U est $C(R_{15})R_{16}$ et A est R_7-Y-.

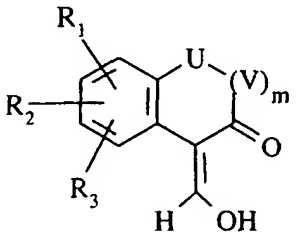
11. Composé selon la revendication 10, dans lequel R_{15} et R_{16} désignent des atomes d'hydrogène, R_7 est méthyle et Y est oxygène.

12. Composés selon la revendication 1, dans lesquels U est $C(R_{15})R_{16}$, m est égal à 0 et R_1 à R_5 et A sont tels que définis dans la revendication 1.

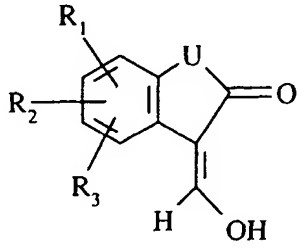
13. Composés selon la revendication 12, dans lesquels R_1 à R_5, R_{15} et R_{16} sont des atomes d'hydrogène et A est R_7-Y-.

14. Composé selon la revendication 13, dans lequel R_7 est méthyle et Y est oxygène.

15. Procédé pour la production de composés de formule I selon la revendication 1, **caractérisé en ce que** l'on fait réagir un composé de formule VIIa ou VIIb

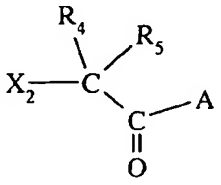


(VIIa) ou



(VIIb),

où R_1 à R_3, U, V et m ont les significations indiquées dans la revendication 1, avec un composé de formule X

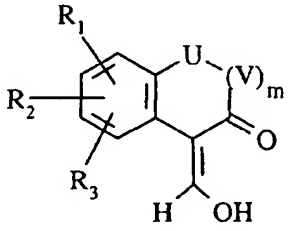


(X),

où R_4, R_5 et A sont tels que définis dans la revendication 1 et X_2 désigne un groupe partant,

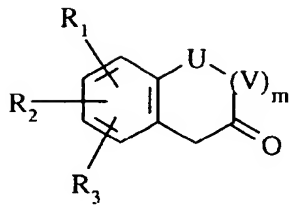
a) en présence d'une base et d'un solvant organique à des températures de 0° à 100°C ou
b) en présence de fluorure de césium en excès dans un solvant organique à des températures de 0° à 50°C.

16. Procédé pour la production de composés de formule VIIa



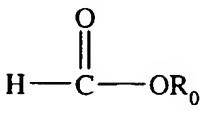
(VIIa),

où R_1 à R_3, U et V ont les significations indiquées dans la revendication 1, et
m est égal à 1, **caractérisé en ce que** l'on fait réagir un composé de formule XIa



(XIa),

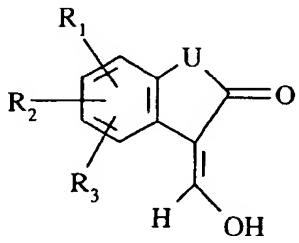
où R_1 à R_3, U, V et m ont les significations indiquées, avec un composé de formule VIII



(VIII),

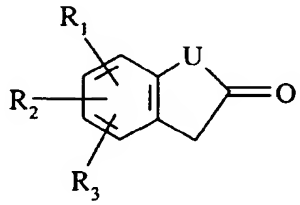
où R_0 est alkyle en C_1-C_4, en présence d'une base et éventuellement d'un solvant organique.

17. Procédé pour la production de composés de formule VIIb



(VIIb),

où R_1 à R_3 et U ont les significations indiquées dans la revendication 1, **caractérisé en ce que** l'on fait réagir un composé de formule XIb

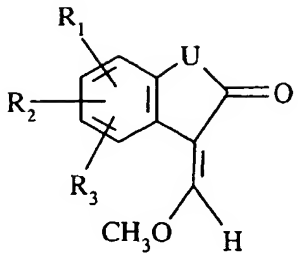


(XIb),

où R_1 à R_3 et U ont les significations indiquées, avec un composé de formule IX

$$H\text{-}C(OCH_3)_3 \qquad (IX),$$

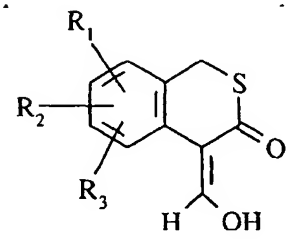
en présence d'un excès d'anhydride d'acide acétique à une température élevée pendant 2 à 24 heures, pour former le comnosé de formule VIIc



(VIIc)

et **en ce que** ce composé subit un clivage d'éther d'énol avec une base aqueuse de 0° à 25°C, et est ensuite traité en conditions acides.

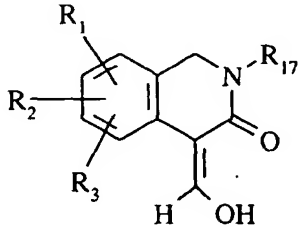
18. Composés de formule $VIIa_1$



($VIIa_1$),

où R_1, R_2 et R_3 ont les significations indiquées dans la revendication 1.

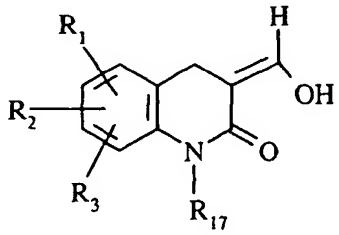
19. Composés de formule $VIIa_2$



($VIIa_2$),

où R_1, R_2, R_3 et R_{17} ont les significations indiquées dans la revendication 1.

20. Composés de formule $VIIa_3$



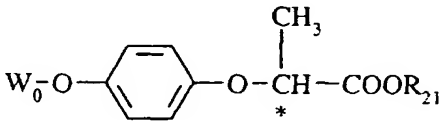
($VIIa_3$),

où R_1, R_2, R_3 et R_{17} ont les significations indiquées dans la revendication 1.

21. Utilisation des composés de formule I en tant qu'antidotes d'herbicides dans des compositions d'herbicides.

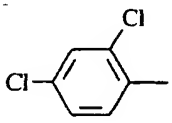
22. Composition ayant une activité herbicide sélective, **caractérisée en ce que**, en plus des adjuvants inertes de formulation habituels, elle contient en tant qu'ingrédient actif un antidote d'herbicide de formule I, selon la revendication 1.

23. Composition ayant une activité herbicide sélective selon la revendication 22, **caractérisée en ce qu'**elle contient un autre ingrédient actif choisi parmi les composés de formules II à VII

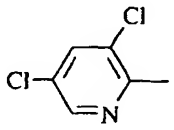


(II),

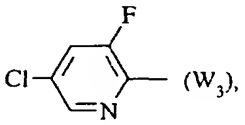
où R_{21} désigne alkyle en C_1-C_4, propargyle ou le groupe $-CH_2-CH_2-O-N=C(CH_3)_2$ et W_0 désigne les groupes



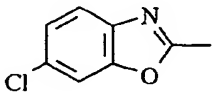
(W_1),



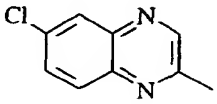
(W_2),



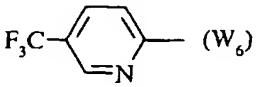
(W_3),



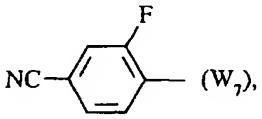
(W_4),



(W_5),

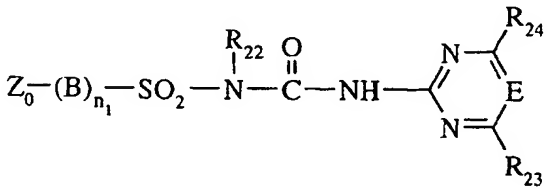


(W_6) ou



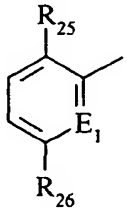
(W_7),

et en particulier les énantiomères R de ces composés ; ou de formule III

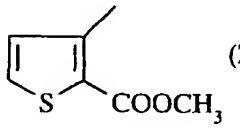


(III),

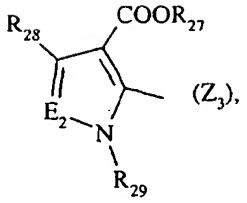
dans laquelle Z_0 représente un groupe

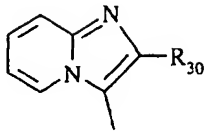


(Z_1),

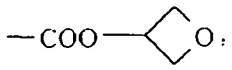


(Z_2),

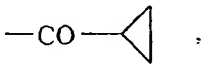

(Z3),


(Z4)

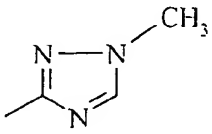
ou CH_3-SO_2- (Z_5) ;
R_{22} signifie hydrogène ou CH_3;
R_{23} signifie CH_3, -OCH_3, -$OCHF_2$, Cl, -$N(CH_3)_2$, -$NHCH_3$, ou CF_3;
R_{24} signifie CH_3, -OCH_3, -$OCHF_2$, -OCH_2CF_3 ou -OC_2H_5 ;
R_{25} signifie -OC_2H_5, -OCH_2CH_2Cl, -$COOCH_3$, -$COOC_2H_5$,


,

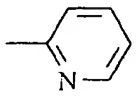
-O-CH_2CH_2-O-CH_3, Cl, -$CON(CH_3)_2$, -$SO_2C_2H_5$, CF_3, -$OCHF_2$,


,

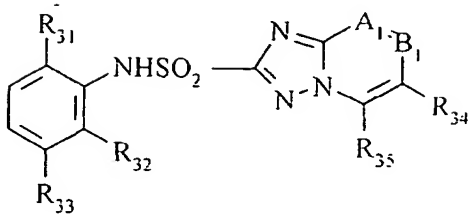
-$N(CH_3)SO_2CH_3$ ou -$N(CH_3)COCH_3$;
R_{26} signifie hydrogène, CH_3, -OCH_3. CF_3, CHF_2 ou -$OCHF_2$;
R_{27} signifie CH_3, C_2H_5 ou le groupe


;

R_{28} signifie hydrogène ou chlore ;
R_{29} signifie CH_3 ou le groupe

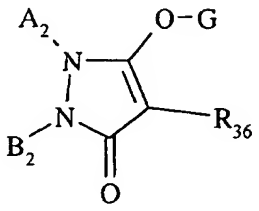

;

R_{30} signifie -$SO_2C_2H_5$ ou chlore ;
E signifie azote ou méthylydine ;
E_1 signifie azote, méthylydine ou C-CH_3 ;
E_2 signifie azote ou méthylydine ;
B signifie oxygène, -NH- ou méthylène ; et
n_1 est égal à 0 ou 1, de même que les sels de ces composés compatibles avec l'agronomie ; ou les composés de formule IV



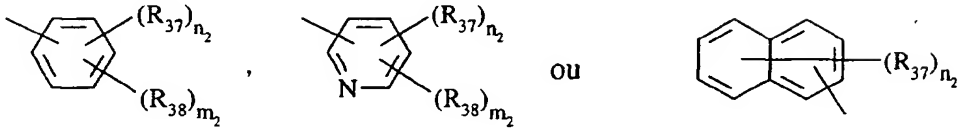
(IV),

où
R_{31} est fluor ou chlore ;
R_{32} est fluor, chlore ou -$COOCH_3$;
R_{33} est hydrogène ou méthyle ;
R_{34} est hydrogène ou fluor ;
R_{35} est hydrogène ou méthoxy ;
A_1 est azote ou C-OC_2H_5 et
B_1 est azote, C-CH_3 ou C-OCH_3 ; ou de formule V

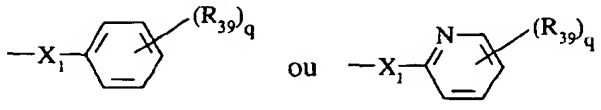


(V),

où
R_{36} représente le groupe



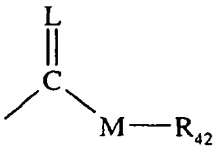
les substituants R_{37}, indépendamment les uns des autres, désignent halogène, nitro, cyano, alkyle en C_1-C_4, halogénoalkyle en C_1-C_4, alcoxy en C_1-C_{10}, halogénoalcoxy en C_1-C_4, (alcényl en C_3-C_6)oxy, (alcoxy en C_1-C_4)-alcoxy en C_2-C_4, (alcynyl en C_3-C_6)oxy, (alkyl en C_1-C_4)carbonyle, (alcoxy en C_1-C_4)carbonyle, (alkyl en C_1-C_4) thio, (alkyl en C_1-C_4)sulfinyle, (alkyl en C_1-C_4)sulfonyle, amino, (alkyl en C_1-C_4)amino ou di(alkyl en C_1-C_4)-amino ;
R_{38} désigne le group



;

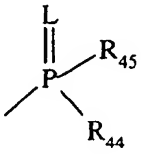
n_2 est égal à 0, 1, 2, 3 ou 4 ;
m_2 est égal à 0 ou 1, la somme de m_2 et n_2 étant égale à 0, 1, 2, 3 ou 4 ;
q est égal à 0, 1, 2 ou 3 ;
X_1 est oxygène, soufre, -CH_2- ou -N(R_{40})- ;
les substituants R_{39}, indépendamment les uns des autres, désignent alkyle en C_1-C_4, halogène, halogénoalkyle en C_1-C_4, alcoxy en C_1-C_4, halogénoalcoxy en C_1-C_4, nitro, cyano, (alcoxy en C_1-C_4)carbonyle, amino, (alkyl en C_1-C_4)-amino ou di(alkyl en C_1-C_4)amino ;

R_{40} désigne hydrogène, alkyle en C_1-C_4, formyl ou (alkyl en C_1-C_4)carbonyle ;
A_2 et B_2, indépendamment l'un de l'autre, signifient hydrogène, alkyle, alcényle, alcynyle, alcoxyalkyle, alkylthioalkyle ou cycloalkyle ou aryle éventuellement substitué ; ou
A_2 et B_2 forment ensemble le reste bivalent d'un système mono-, bi-, tri- ou polycyclique saturé ou insaturé et éventuellement substitué ;
G désigne hydrogène ou les groupes -CO-R_{41} (a),

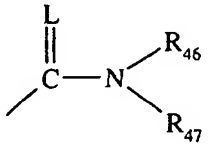


(b),

-SO_2-R_{43} (c),

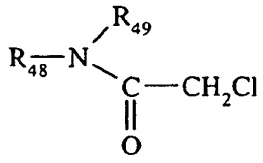


(d),



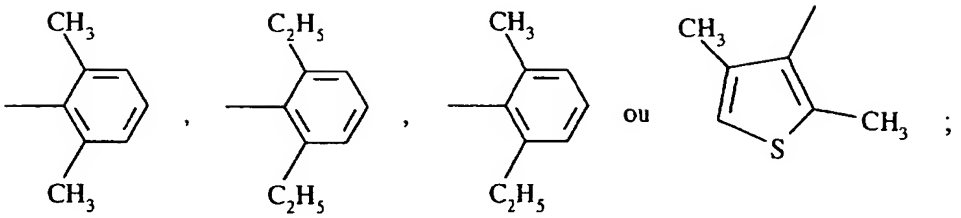
(e),

ou M_1 (f)
L et M, indépendamment l'un de l'autre, sont oxygène ou soufre ;
R_{41} est halogénoalkyle, alcényle, alcoxyalkyle, alkylthioalkyle, polyalcoxyalkyle ou cycloalkyle, qui peut contenir des hétéroatomes, phényle éventuellement substitué, phénylalkyle éventuellement substitué, hétéroaryle substitué, phénoxyalkyle substitué ou hétéroaryloxyalkyle substitué ;
R_{42} est halogénoalkyle, alcényle, alcoxyalkyle ou polyalcoxyalkyle ou phényle ou benzyle éventuellement substitués ;
R_{43}, R_{44} et R_{45}, indépendamment les uns des autres, sont alkyle, halogénoalkyle, alcoxy, alkylamino, dialkylamino, alkylthio, alcénylthio, alcynylthio ou cycloalkylthio ou phényle, phénoxy ou phénylthio éventuellement substitués ;
R_{46} et R_{47}, indépendamment l'un de l'autre, sont hydrogène, alkyle, halogénoalkyle, alcényle, alcoxy ou alcoxyalkyle, phényle ou benzyle éventuellement substitués ; ou
R_{46} et R_{47} forment ensemble un reste alkylène, pouvant éventuellement contenir de l'oxygène en tant qu'hétéroatome ; et
M_1 désigne un ion métallique équivalent ou un ion ammonium, ainsi que les sels et les diastéréoisomères des composés de formule V ; ou de formule VI



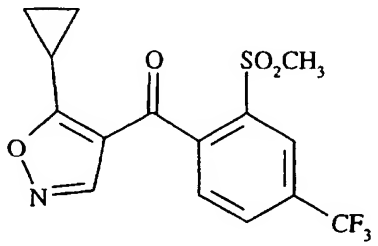
(VI),

où R_{48} désigne un groupe



et

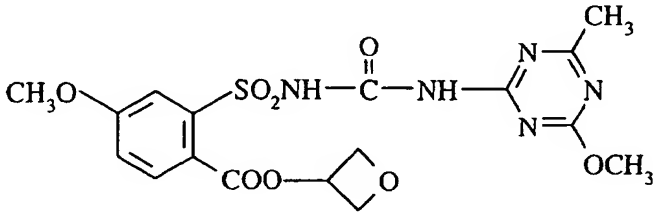
R_{49} désigne un groupe $-CH(CH_3)CH_2OCH_3$, $-CH_2OCH_3$ ou $-CH_2OC_2H_5$; ou de formule VII



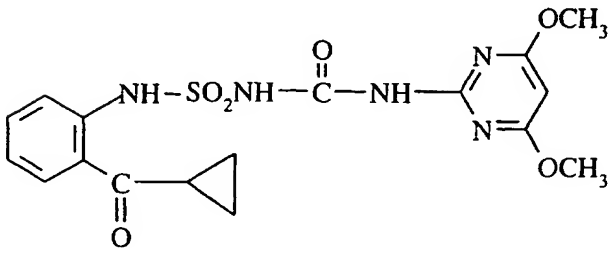
(VII)

24. Composition selon la revendication 23, **caractérisée en ce qu'**elle contient du clodinafop, du quizalafop, du propaquizafop, du fénoxaprop, du fluazifop et du cyhalofop en tant qu'herbicides de formule II.

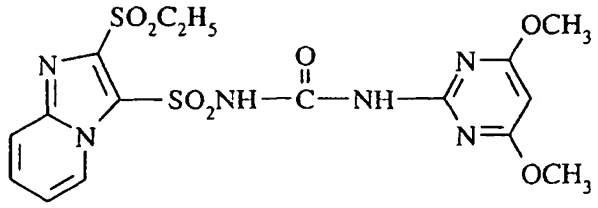
25. Composition selon la revendication 23, **caractérisée en ce qu'**elle contient du tribénuron, du metsulfuron, du primisulfuron, de l'éthametsulfuron, du sulfométuron, du chlorimuron, de l'oxasulfuron, du triasulfuron, du cinosulfuron, du triflusulfuron, du bensulfuron, de l'éthoxysulfuron, du sulfazuron, du nicosulfuron, du rimsulfuron, du flupyrsulfuron, du thifensulfuron, du clopyrazosulfuron, du pyrazosulfuron, du sulfosulfuron, de l'azimsulfuron et de l'amidosulfuron en tant qu'herbicides de formule III, ainsi que les composés de formules IIIa à IIId



(IIIa),

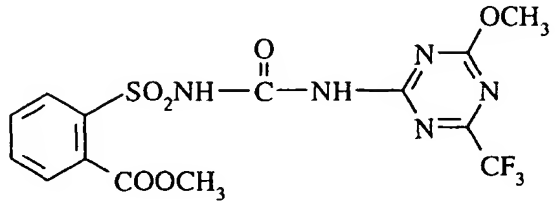


(IIIb),



(IIIc)

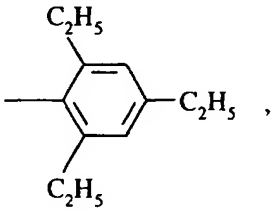
et



(IIId).

26. Composition selon la revendication 23, **caractérisée en ce qu'**elle contient du flumetsulam, du métosulam et du cloransulam en tant que composés de formule IV.

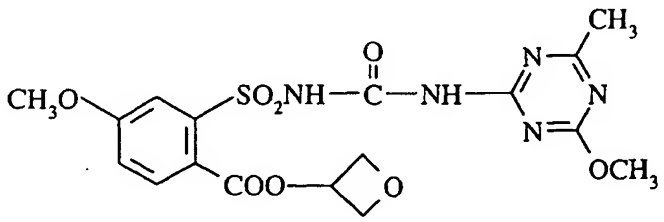
27. Composition selon la revendication 23, **caractérisée en ce que** dans le composé de formule V, R_{36} est mésitylényle ou



A_2 et B_2 sont des groupes méthyle ; ou A_2 et B_2 forment ensemble un groupe $-(CH_2)_4-$; et G désigne hydrogène ou $-COC(CH_3)_3$.

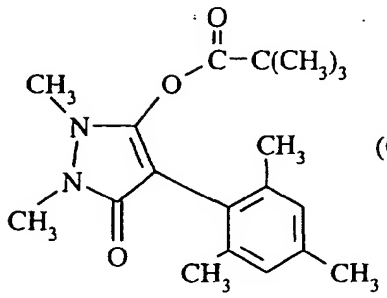
28. Composition selon la revendication 23, **caractérisée en ce qu'**elle contient en tant que composé de formule VI du métolachlor, de l'alachlor, de l'acétochlor, du diméthénamide, et en particulier la aRS, 1'S(-)N-(1'-méthyl-2'-méthoxyéthyl)-N-chloroacétyl-2-éthyl-6-méthyl-aniline.

29. Composition selon la revendication 23, **caractérisée en ce qu'**elle contient en tant que composé de formule I l'ester de méthyle de l'acide (3-oxoisochroman-4-ylidèneméthoxy)acétique (composé n° 01.002) ou l'ester de méthyle de l'acide (2-oxoindan-1-ylidèneméthoxy)acétique (composé n° 02.004), et en tant qu'ingrédient actif de formule II le clodinafop, en tant qu'ingrédients actifs de formule III le primisulfuron, le chlorimuron ou le composé de formule



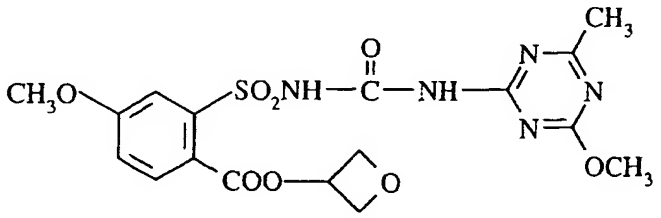
(IIIa),

et en tant qu'ingrédient actif de formule V le composé de formule



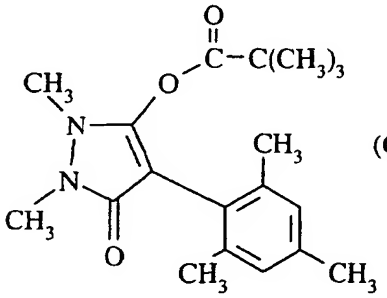
(Composé n° 1.3).

30. Composition selon la revendication 23, **caractérisée en ce qu'**elle contient en tant que composé de formule I l'ester de méthyle de l'acide (3-oxoisochroman-4-ylidèneméthoxy)acétique (composé n° 01.002), l'ester de méthyle de l'acide (2-oxoindan-1-ylidèneméthoxy)acétique (composé n° 02.004) ou l'ester de méthyle de l'acide (3-oxoisothiochroman-4-ylidèneméthoxy)acétique (composé n° 01.007), et en tant qu'ingrédient actif de formule II le clodinafop, en tant qu'ingrédients actifs de formule III le primisulfuron, le chlorimuron ou le composé de formule



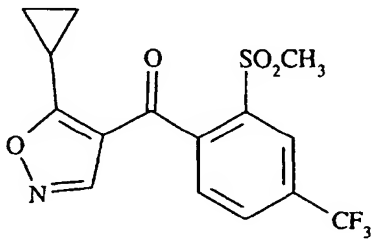
(IIIa),

et en tant qu'ingrédient actif de formule V le composé de formule



(Composé n° 1.3).

et en tant qu'ingrédient actif le composé de formule VII



(VII).

31. Procédé pour la lutte sélective contre les mauvaises herbes et les herbes dans les cultures de plantes utiles **caractérisé en ce que** les plantes utiles, leurs semences ou leurs boutures ou les zones de leur culture sont traitées simultanément ou séparément par une quantité efficace en tant qu'herbicide d'un herbicide de formule II, III, IV, V, VI ou VII selon la revendication 23 et par une quantité active en tant qu'antagoniste d'herbicide d'un antidote de formule I selon la revendication 1.

32. Procédé selon la revendication 31, **caractérisé en ce que** les cultures de plantes utiles ou les zones de culture pour les cultures de plantes utiles sont traitées par 0,001 à 2 kg/ha d'un herbicide de formule II, III, IV, V, VI ou VII et par une quantité de 0,001 à 0,5 kg/ha d'un antidote de formule I.

33. Procédé selon la revendication 31, **caractérisé en ce que** les cultures de plantes utiles concernées sont celles de maïs, de céréales, de soja ou de riz.